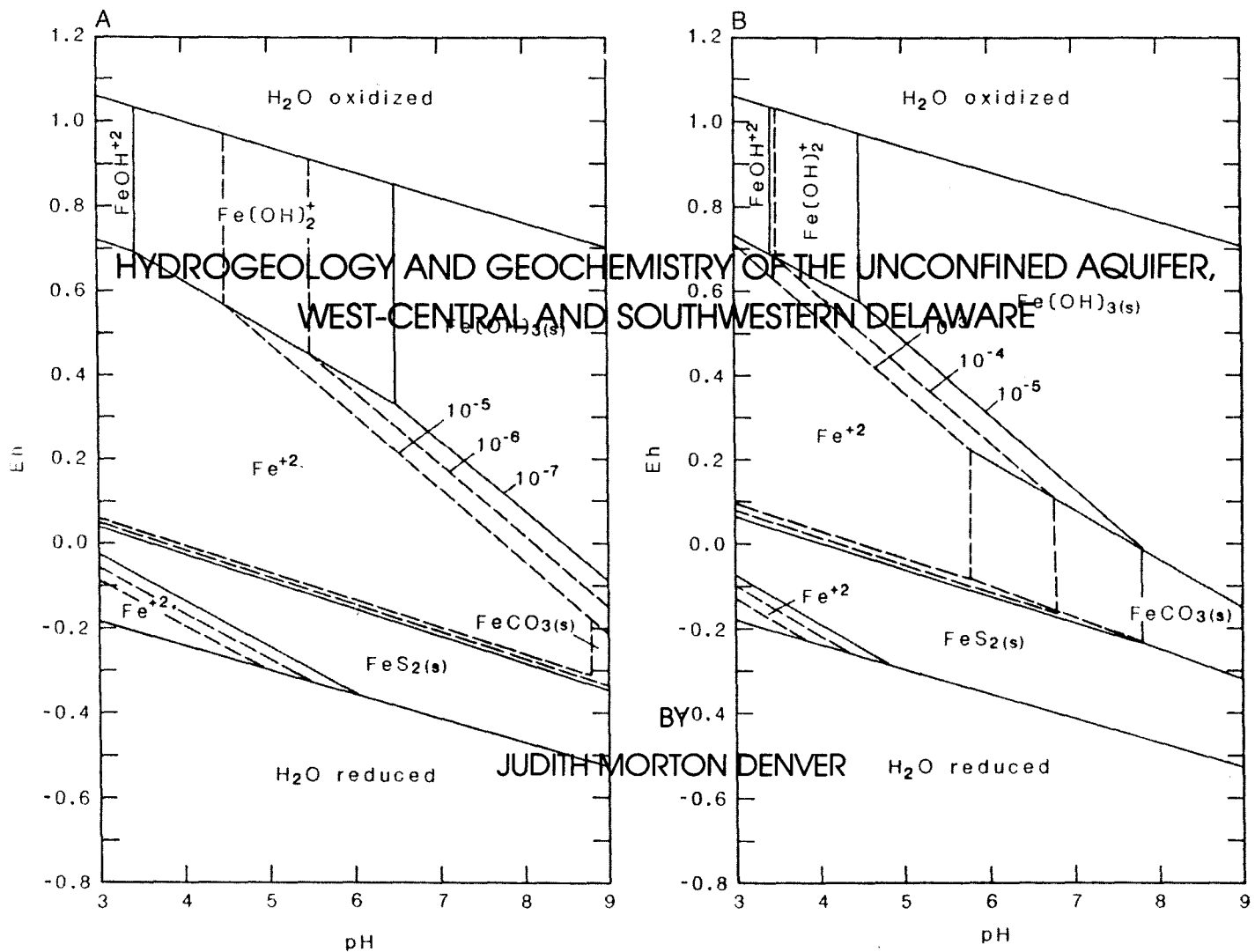


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HYDROGEOLOGY AND GEOCHEMISTRY OF THE UNCONFINED AQUIFER,  
WEST-CENTRAL AND SOUTHWESTERN DELAWARE

by

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HYDROGEOLOGY AND GEOCHEMISTRY OF THE UNCONFINED AQUIFER,  
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ABSTRACT

The unconfined aquifer is the major source of water supply in west-central and southwestern Delaware. The aquifer, which is composed of quartz sand, gravel, clay, and silt, ranges in thickness from 20 to 200 feet. The water table ranges from land surface to about 20 feet below land surface. Analyses of water from wells distributed throughout the area were used to study processes controlling the chemical quality of the water in the unconfined aquifer.

Mass-balance calculations showed that the chemistry of ground water unaffected by human activities seems to result from dissolution of feldspars (plagioclase and orthoclase) and biotite by atmospheric precipitation. Concentrations of the major ions (sodium and bicarbonate) range from 4.4 to 10.0 mg/L (milligrams per liter) and from 5.8 to 52.4 mg/L, respectively. Ferrous iron may also be a major ion where the aquifer has a reducing environment. Concentrations of chemical constituents in the unconfined aquifer are naturally low and specific conductance of the water sampled was less than 100  $\mu\text{S}/\text{cm}$  (microsiemens per centimeter at 25° Celsius).

Chemistry of water in the unconfined aquifer is closely related to land use. For example, the application of nitrogen species, crushed dolomite, and potassium chloride to farmland is directly related to concentrations of nitrate, chloride, calcium plus magnesium, and potassium in ground water. The concentration of bicarbonate ions is apparently depleted by reaction with the hydrogen ions produced during nitrification.

The permeability and drainage of soil which control redox potential near the surface of the aquifer also influence water chemistry. Most of the soils are well drained so that chemicals applied to or near the land surface are carried rapidly into the aquifer. Thus, even small changes in water chemistry can be significant.

Elevated concentration of nitrate is the major water-quality problem in the oxygenated parts of the aquifer. Agricultural applications of inorganic fertilizer and manure are

the most widespread sources of nitrate. Leachate from animal confinement and domestic septic systems are other sources of nitrate in the water.

Two characteristic trends in the chemistry of water in the unconfined aquifer are (1) increasing alkalinity with increasing specific conductance associated with oxygenated natural water and reduced water and (2) consistently low alkalinity (less than 10 mg/L) over a wide range of specific conductance associated with oxygenated water influenced by land use. Concentration of nitrate is usually greater than 10 mg/L when the specific conductance is greater than 120  $\mu$ S/cm and alkalinity is less than 10 mg/L. Thus, determinations of specific conductance and alkalinity in the field can be used to describe the water quality in the aquifer.

## INTRODUCTION

### Background

The unconfined aquifer consists largely of the Columbia and Beaverdam formations (Jordan and Smith, 1983) and, in some places, the subcrop of the Manokin and Frederica aquifers. It is the major source of water in west-central and southwestern Delaware and of recharge to deeper confined aquifers. Concentrations of chemical constituents in the water, nitrate and iron in particular, are locally high enough to restrict use of the water. The sources of chemical constituents in the water and the reactions that control their concentrations and mobilities determine the distribution of these constituents in the ground-water system.

The study area includes about 540 square miles in the central part of the Delmarva Peninsula (Figure 1). The boundaries are the Delaware border to the west and south, and the Chesapeake Bay-Delaware Bay and Chesapeake Bay-Atlantic Ocean drainage divides to the east. Thickness of the unconfined aquifer generally ranges from 20 feet in the north to 200 feet in the south.

### Purpose and Scope

The purpose of this report is to describe the hydrology and to define the water chemistry of the unconfined aquifer and the geochemical processes and other factors that control the chemical quality of the water.

The conclusions of the study are based on chemical analyses of water from 121 wells, including domestic, observation, municipal, industrial, irrigation, and other agricultural wells. Water samples were collected from June 1982 to October 1983 from wells distributed throughout the area (Figure 2A). Subjects discussed in the report include (1) geologic framework and hydrology of the unconfined aquifer; (2) geochemical and anthropogenic (human) influences on ground-water chemistry; (3) relation of concentrations of major ions in ground water to geology, hydrology, soil, and land use at the well sites; (4) changes in water chemistry resulting from variations of depth and pumpage; (5) trends in data obtained in the field and the laboratory; and (6) relations of mineral equilibria.

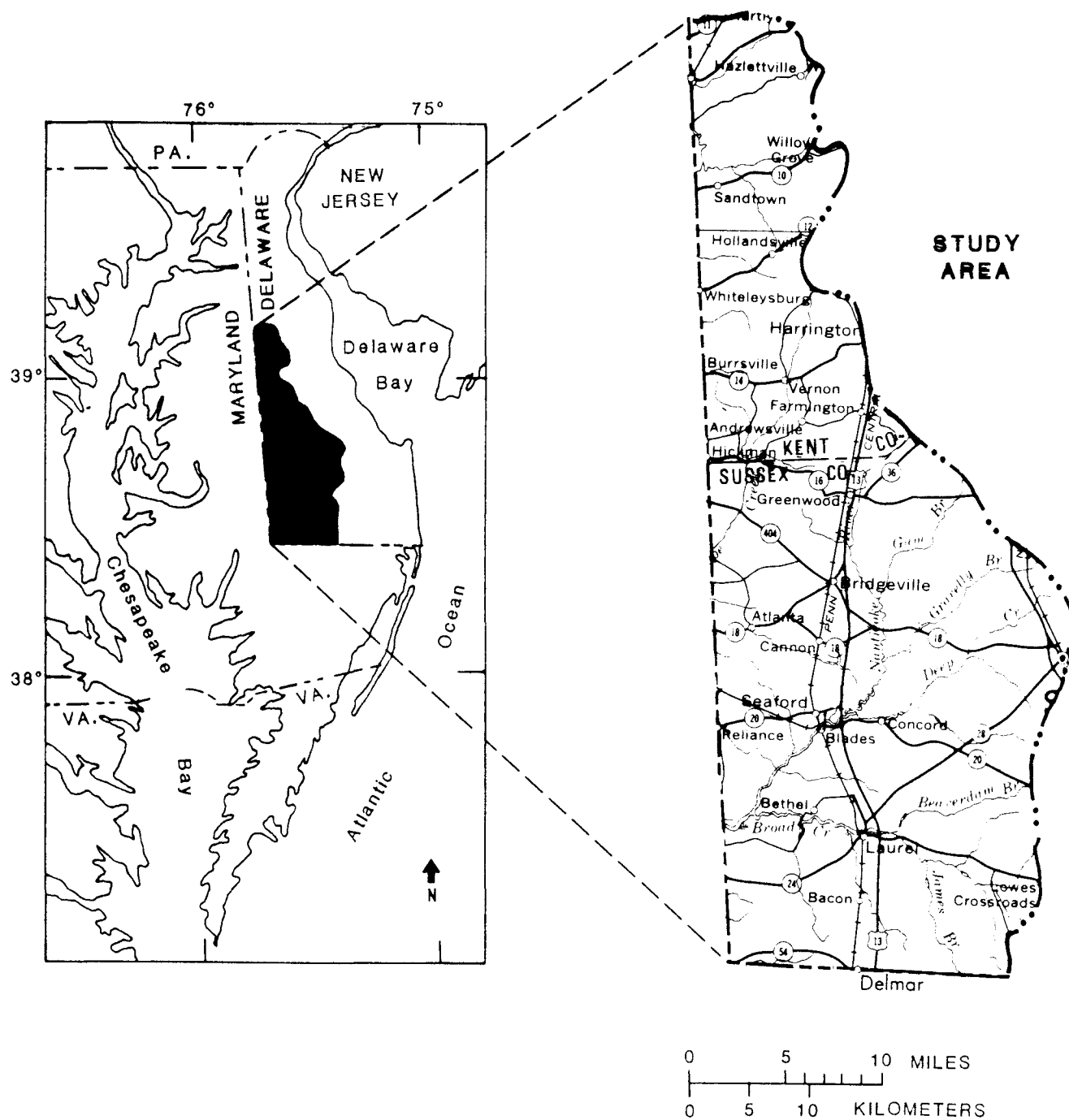


Figure 1. Location of study area.

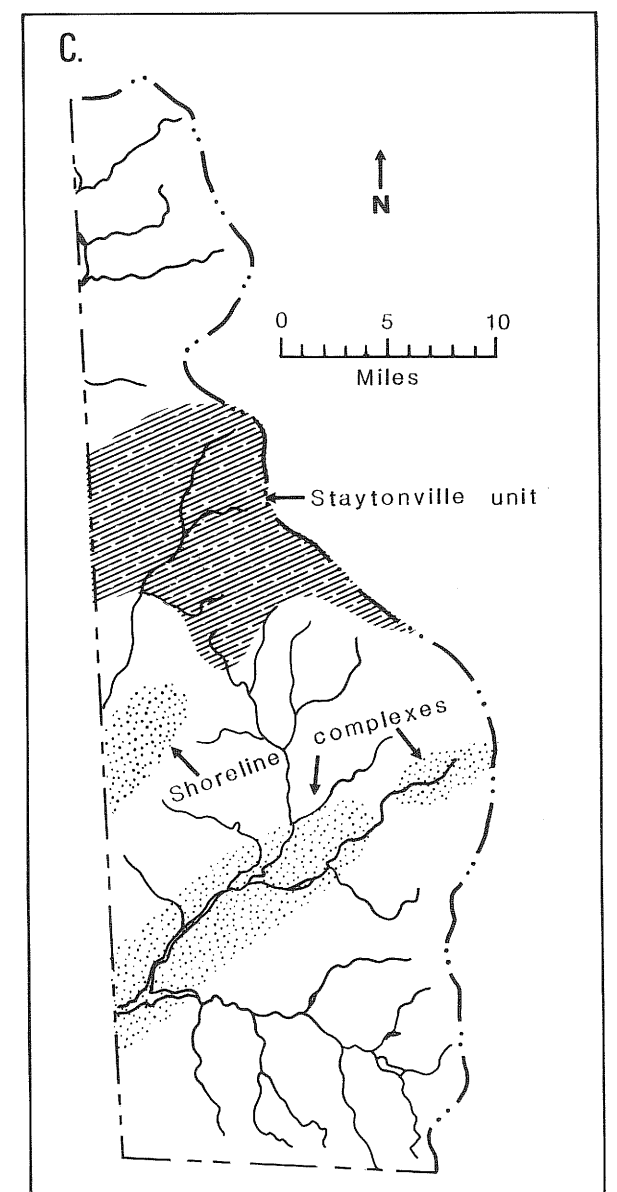


Figure 2. Locations of wells sampled for chemical analyses, trace of geologic section, and distribution of geologic units composing the unconfined aquifer.

Methods of Study

## Well Sampling

The numbers and the types of wells sampled are shown in Table 1. Selection of wells for sampling was based on the availability of wells equipped with pumping and sampling mechanisms that introduced the least amount of oxygen into the sample. Most of the wells sampled are irrigation and farm-supply wells equipped with deep turbine pumps and taps on the wellhead. These wells were abundant and suitable for sampling. Clusters of piezometers (referred to as "test wells" in the remainder of the report) were installed at three sites for sampling water at various depths in the aquifer (shown in Figure 2). Wells known to be contaminated by leachate from landfills and other types of waste were not sampled.

TABLE 1. Wells selected for chemical sampling.

Type of well	Number of wells	
	Laboratory and field data	Field data only
Irrigation	15	4
Agricultural, other	27	16
Municipal and public	7	2
Domestic	7	58
Observation or test	12	1
Industrial	2	0

### Chemical Analysis

Specific conductance, pH, alkalinity, dissolved oxygen, and water temperature were measured in the field at 121 wells (Table 10, Appendix I). Water samples were also collected at 50 of these wells for laboratory determination of concentrations of major ions, trace metals, nutrients, and total organic carbon (Table 11, Appendix I). Samples collected at two different times from eight test wells were analyzed at the U.S. Geological Survey National Water Quality Laboratory in Doraville, Georgia. Samples collected from the wells at least four times over a 1-year period were analyzed in the field. Sampling procedures used are described by Skougstad and others (1979).

### Acknowledgments

This report was prepared under a cooperative agreement between the Delaware Geological Survey and the U.S. Geological Survey. The staff of the Delaware Geological Survey, under the direction of Robert R. Jordan, provided well records and drilling and geophysical logging of test wells.

The Delaware Department of Natural Resources and Environmental Control Water Supply Branch, the Delaware Department of Health and Social Services Division of Public Health, and the Delmarva Drilling Company, Inc.<sup>1</sup>, provided access to their files of well data and helped locate wells suitable for sampling.

Special thanks are extended to the many homeowners, farmers, municipalities, businesses, and industries who allowed their wells to be sampled.

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<sup>1</sup>/The use of brand or company names in this report is for identification purposes only and does not constitute an endorsement by the U.S. Geological Survey.



## GEOLOGIC FRAMEWORK

### Regional Setting

The Delmarva Peninsula is part of the Atlantic Coastal Plain Province. The Coastal Plain consists of a seaward-dipping wedge of unconsolidated and semiconsolidated sediments that range in age from Jurassic to Holocene. The sediments that compose the Delmarva Peninsula were deposited in a subsiding basin generally referred to as the Salisbury Embayment (Richards, 1948). The dips of the sediments are generally less steep in successively younger units and most of the units thicken seaward.

The units of primary interest are the uppermost ones: the Columbia Formation, the informally designated Staytonville unit, the Beaverdam Formation, and the shoreline complexes. In Delaware these units are of Pliocene and Pleistocene age (Jordan and Smith, 1983) and are referred to here as "surficial." The base of the Columbia Formation is an erosional angular unconformity that truncates underlying sediments of the Chesapeake Group of Miocene age. Sand units in the Chesapeake Group are of interest where they subcrop the surficial sediments and act as part of the unconfined aquifer.

### General Stratigraphy

#### Chesapeake Group

The Chesapeake Group is a marine and marginal-marine sequence that consists predominantly of gray and bluish-gray silt, interbeds of fine- to medium-grained sand, and some shell beds (Jordan, 1962).

The Manokin aquifer is the only aquifer of the Chesapeake Group in the study area that is a significant part of the unconfined aquifer. Its subcrop area is extensive in Sussex County (Figure 2B).

#### Columbia Formation

The Columbia Formation (Jordan and Smith, 1983) is a fluvial sequence of sediments that first filled channels cut into the Chesapeake Group and later spread laterally to form a coalescing sheet of sand. Sediments of the Columbia Formation are primarily medium- to coarse-grained sand and gravel, but some layers of clay and silt are also present. The coarseness of the sediments varies, but generally decreases downcurrent (Jordan, 1964). The

sand grains are typically stained with limonite, and limonite crusts are common, particularly at the base of the unit. The rusty-brown to orange coating on the sand grains is indicative of deposition in a subaerial, oxidizing environment.

#### Beaverdam Formation

The Beaverdam Formation is of fluvial and possibly estuarine origin (Jordan, 1967). Rasmussen and Slaughter (1955, p. 113) described the Beaverdam as ". . . unconsolidated, white to buff, medium-grained, quartz sand, with small quantities of coarse and fine sand, pebbles, granules, and white silt." Thin clay-silt beds are common throughout the formation. The Beaverdam is generally finer grained and better sorted than the Columbia Formation. Exposures of the Beaverdam may have enough clay-silt matrix to bind the sand grains into a semiconsolidated mass (Owens and Denny, 1979).

#### Staytonville Unit

Jordan (1967) identified deposits informally known as the Staytonville unit overlying the Columbia Formation of southwestern Kent and northwestern Sussex counties (Figure 2C). It consists primarily of medium-grained sand, but contains some fine and coarse sand and silt. The unit probably represents estuarine deposition. Irregular and indistinct bedding and abrupt lateral and vertical changes in color distinguish it from the underlying Columbia Formation. Maximum thickness of the Staytonville unit is about 45 feet.

#### Shoreline Complexes

The shoreline complexes include a variety of sediments associated with former beach deposits; for example, beach proper, dunes, lagoons, bars(?), and inner-neritic environments (Jordan, 1964). These sediments overlie the Beaverdam Formation (Jordan, 1967).

There are two major shoreline complexes in the study area: one parallel to the Nanticoke River and another parallel to Marshyhope Creek (Figure 2C).

### Mineralogy

Jordan (1964) found that the basic mineralogic composition of all the surficial units is similar, with the primary differences being in texture and sedimentary structure. The sands are subarkosic and the gravel consists primarily of vein quartz, sandstone, quartzite, and chert. The average composition of the sands is 80 percent quartz and 18 percent feldspar. Orthoclase content is generally five times that of plagioclase. The average muscovite content is about 0.5 percent, but varies considerably.

The heavy mineral content of the surficial sediments is usually less than 1 percent, and 77 percent are opaque. The most common nonopaque, heavy minerals are zircon, epidote, amphibole, sillimanite, tourmaline, and staurolite. Jordan (1964) considered the heavy mineral content of the sands to be consistent overall and to be virtually a single suite with some variations.

The major minerals in the subcropping aquifers of the Chesapeake Group are quartz and, to a lesser degree, feldspar. Hornblende is the predominant nonopaque heavy mineral (Owens and Denny, 1979).

### Sedimentary Units

The Columbia Formation fills erosional channels that were cut into the underlying Chesapeake Group in a period of marine regression during glaciation. Jordan and Smith (1983) suggest that this regression could have occurred as early as the Pliocene Epoch. As sea level rose during subsequent marine transgression and streams began to aggrade, the surficial Columbia sediments were reworked and a sequence of fluvial, bay, and shoreline facies were deposited (Jordan, 1967). Jordan postulates that a major stream system discharged to the ocean and that the shoreline interface changed position with time as sea level changed.

A geologic section (Figure 3) from north to south shows the general characteristics of the surficial sediments and the subcrop area of the Manokin aquifer of the Chesapeake Group. Gamma logs were the principal control used to construct the section.

The surficial deposits in Kent County consist almost entirely of the fluvial Columbia Formation (section A-A' in Figure 3). In Sussex County, however, the Beaverdam Formation overlies the Columbia Formation (Figures 2C and 3) and the surficial deposits are more complex owing to the variation in depositional environments from fluvial to shoreline complexes.

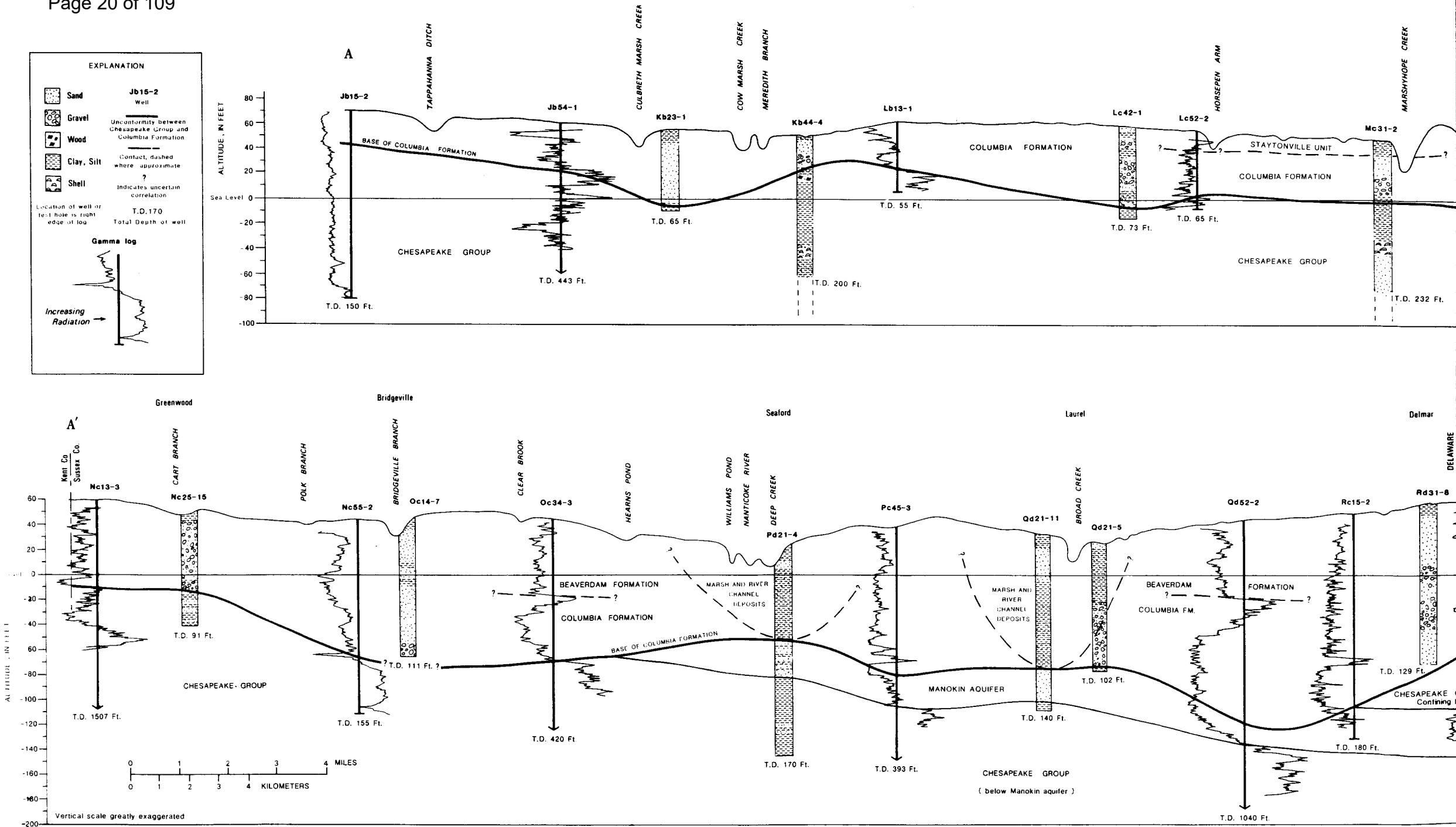


Figure 3. Geologic sections showing the configuration of the major geologic units of the unconfined aquifer.

The channeled nature of the base of the Columbia Formation is evident on the section.

Differentiation between the Beaverdam and Columbia formations is difficult because of mineralogic similarities. However, the Beaverdam has a fine-grained matrix material that is absent in the Columbia Formation. On this basis, and because of changes in color noted in the geologic and drillers' logs, some differentiation between the two units is shown in Figure 3. In the logs of section A' to A" (Figure 3) sediments identified as Beaverdam have a slightly higher gamma ray count than those of the Columbia Formation. These differences are most noticeable for wells Oc34-3 and Qd52-2. The sand above the clay layer exhibits characteristics of the Beaverdam Formation and the coarser sand below the clay is identified as the Columbia Formation. The clay layer shown between the sand units is included as part of the Columbia Formation because of the gradual change from coarse- to fine-grained sediments. The sharp contact between the Beaverdam Formation and the top of the clay seems to be erosional. A fine-grained sand overlying a coarse sand is also shown in other logs.

The subcrop of the Manokin aquifer (shaded area beneath the Columbia in Figure 3) extends from well Pd21-4 at Seaford to well Rc15-2 near the Delaware-Maryland boundary. Other less extensive Miocene aquifers may subcrop the surficial sediments north of Pd21-4, but these were not evident from the logs used in the section.

The lithology of the Columbia deposits is commonly similar to the sands of the Chesapeake Group and the contact between them can be difficult to distinguish. Sundstrom and Pickett (1970) note that the Chesapeake sands are usually grayer and better sorted than the Columbia sediments.

Clay-silt layers are common but not laterally continuous within the Columbia and Beaverdam deposits. Thick, predominantly clay-silt deposits also underlie the major waterways in Sussex County. These deposits are delineated in geologic section A'-A" (Figure 3) based on logs obtained around Seaford and Laurel, Del. They are associated with the Nanticoke River and Broad Creek and are Holocene marsh deposits. Organic clays and wood are found in cuttings from wells drilled in these areas.

The Staytonville unit was identified in the top 12 to 18 feet of boring Nc13-3 (section A'-A", Figure 3) by Talley (1975). The silty, fine sands in the surficial section of Mc31-2 and Lc52-2 (section A-A', Figure 3) are also probably the Staytonville unit.

## HYDROGEOLOGY OF THE UNCONFINED AQUIFER

### Definition

The unconfined aquifer includes the surficial deposits and underlying sands of the Manokin aquifer of the Chesapeake Group, where present. Other minor sands of Miocene age with smaller subcrops are not included as part of the unconfined aquifer owing to scant data on their areal extent.

### Base of Aquifer

The altitude of the base of the unconfined aquifer (Figure 4) generally ranges from 50 feet above sea level in the northern part of the study area to 150 feet below sea level in the southern part. The irregular, channeled nature of the base is evident from Figure 4 even though data points are too far apart for mapping the channels in detail.

The greatest depths to the base of the aquifer are in two major areas: near Delmar, Del., and near the eastern edge of the study area south of the Kent-Sussex County line. The aquifer includes the Manokin sands in these areas. The depth to the base of the Columbia Formation in the two areas is probably attributable to a high degree of erosion of the Chesapeake Group in the sandy area of subcrops.

### Thickness

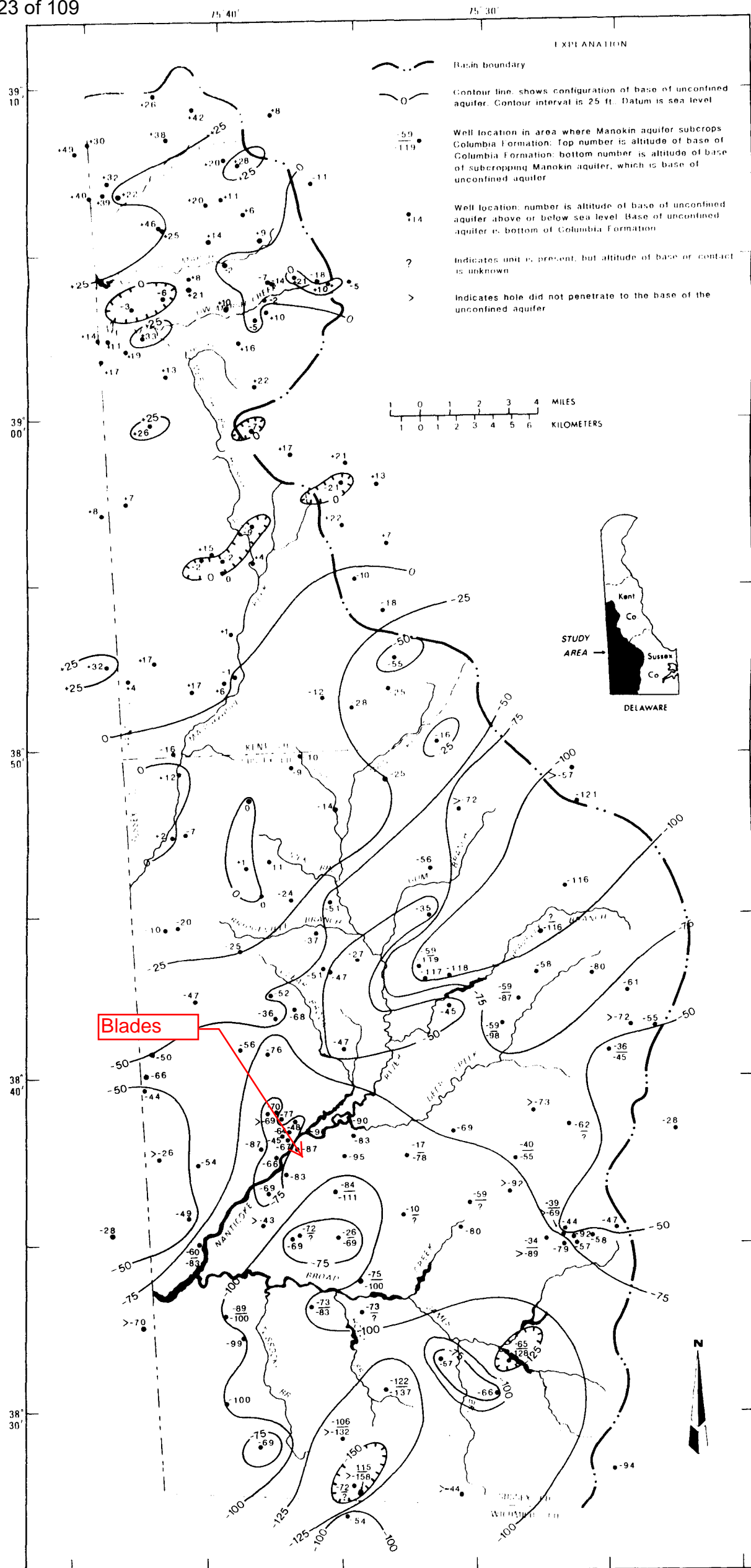
The thickness of the unconfined aquifer (Figure 5) generally ranges from 20 feet in the northern part of the area to 200 feet in the southern part. Part of the thickness of the aquifer is neither sandy nor suitable for wells because the aquifer contains clays and silts of the surficial deposits and is not fully saturated.

### Hydrology

#### Depth to Water and Saturated Thickness

The depth to the water-table surface generally ranges from land surface to 20 feet below land surface. In most of the area, it is usually between 5 and 10 feet below land surface. Therefore, the saturated thickness of the sediments in the unconfined aquifer is nearly the total thickness of the sediments. The unsaturated zone can be a significant part of the total thickness

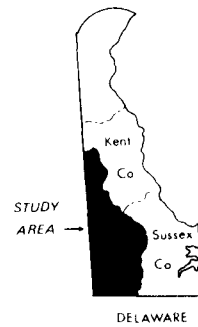
Figure 4. Configuration of the base of the unconfined aquifer.



EXPLANATION

- Basin boundary
- Line of equal thickness. Contour interval is 25 ft.
- Well location and thickness, in feet, of unconfined aquifer from land surface to base of Manokin aquifer in areas where Manokin aquifer subcrops the Columbia Formation. Top number is thickness of surficial sediments, including Columbia Formation, Staytonville unit, Beaverdam Formation, and shoreline complexes. Bottom number is thickness of surficial sediments and subcropping Manokin aquifer
- Well location and thickness, in feet, of unconfined aquifer from land surface to base of Columbia Formation
- Indicates unit is present but thickness is unknown
- Indicates hole did not penetrate to the base of the unconfined aquifer

1 0 1 2 3 4 MILES  
1 0 1 2 3 4 5 6 KILOMETERS



Blades, DE



Figure 5. Thickness of the unconfined aquifer.



in the northern part of the area where the aquifer is less than 40 feet thick.

### Ground-Water Recharge and Discharge

The upper surface of the water table is generally parallel to the topography of the land surface. High elevations are generally recharge areas and low elevations along streams and rivers are discharge areas. Discharge areas are a much smaller percentage of the surface area of the drainage basins than recharge areas.

Johnston (1973), in a study of unconfined aquifer hydrology in Delaware, found that most recharge to the unconfined aquifer is from precipitation and most discharge is seepage to surface-water bodies. The long-term recharge rate averages about 14 inches per year. Most recharge occurs during the non-growing season from mid-October to early April. During this time, the water table generally rises. From April to mid-October, when recharge is less frequent and evapotranspiration is high, water levels generally decline.

Streams incised into the upper part of the aquifer derive 75 percent of their flow from ground-water discharge. Johnston (1973) calculated that pumpage from the entire unconfined aquifer in 1970 was small compared to natural discharge: Withdrawal by pumpage was 33 million gallons per day (Mgal/day), and the discharge rate to streams was 800 Mgal/day. Johnston calculated that over the long term, the average discharge from the aquifer is equal to the average recharge.

Recharge to and from the Chesapeake Group aquifers below the surficial deposits is considered to be very small relative to the total amount of water recharging the unconfined aquifer and discharging to streams (Johnston, 1977).

### Ground-Water Flow Patterns

The relief of the land surface, aquifer thickness, lithology, pumpage, and aquifer boundaries affect the ground-water flow system. The boundaries of the study area to the east and north of the Delaware state line are based on ground-water drainage divides. The drainage basins included are those discharging to the Nanticoke and Choptank river systems in Delaware.

Local flow systems are more likely to reach the base of the aquifer where the aquifer thickness is small, as in the northern

part of the area. Thus, small independent flow cells are developed. In the southern part of the area, where the aquifer is much thicker, the flow system is more complex. Here, small, shallow flow cells are developed between recharge areas and small streams and ditches. There are also longer flow paths in the south extending from the ground-water divides, along the base of the aquifer, to sites along major rivers. The unconfined aquifer also recharges subcropping aquifers in the Chesapeake Group such as the Manokin. Water may leak upward through the confining bed where artesian head in the confined parts of these aquifers is greater than water-table head.

### Hydraulic Characteristics

The hydraulic characteristics of the unconfined aquifer in Delaware are summarized by Johnston (1973). The transmissivity of the sediments is variable and is related to changes in lithology and the southward increase in saturated thickness. The average transmissivity is 9,500 ft<sup>2</sup>/d based on a digital model in an area adjacent to this study (Johnston, 1977). Generally, the transmissivity of the aquifer is typical of values representing a medium to coarse sand. The average hydraulic conductivity of the aquifer is about 90 feet per day (ft/d).

### Properties of Soils

The properties of the soils in the upper part of the aquifer should be considered because the water table is generally within a few feet of the land surface. The soil surveys of Kent and Sussex counties in Delaware, prepared by the U.S. Department of Agriculture (1971 and 1974), are the source of soils information for this study.

The parent materials from which soils are formed affect their texture. Soils of the Evesboro series, an excessively drained soil, were formed in coarse-textured sediments consisting mostly of sand, but containing some silt and clay. Parent material of the other soils in the area consisted mainly of sand containing significant amounts of clay and some silt. As the content of clay and silt increases, soil drainage decreases. The permeabilities of soils and the ability of soils to hold moisture are related to the proportions of sand, clay, and silt in the soils.

Soil drainage affects processes that influence ground-water quality: the accumulation of organic matter, chemical weathering of silicate minerals to clays, and the reduction and transfer

of iron. These factors will be discussed in more detail in the following section.

Well and excessively well-drained soils, such as Evesboro and Rumford, are most widespread in the southern part of the study area. Poorly drained soils, such as Pocomoke and Fallsington, predominate in the Kent County part.

## GEOCHEMICAL FACTORS AFFECTING WATER CHEMISTRY IN THE UNCONFINED AQUIFER

### Precipitation

Primary recharge to the unconfined aquifer is by infiltration of precipitation through the soil zone. The average annual precipitation in southwestern Delaware is 43 inches and the average annual recharge of the aquifer is 14 inches (Johnston, 1973). The average dissolved solids concentration of precipitation collected at a station in Lewes, Del., from August 1978 to January 1983, was 6.8 mg/L (T. M. Church, written commun., 1983). The volume-weighted pH of the precipitation averaged 4.34. The chemical composition of precipitation is presented in Table 2. The average dissolved-solids concentration of precipitation entering the aquifer is 20 mg/L after evaporation to about one-third of its original volume (Cushing and others, 1973).

### Oxidation and Reduction Reactions

The tendency of a ground-water system is to change from an oxidizing (oxic) to a reducing (anoxic) system. The rate of oxygen depletion and the degree of reduction in the unconfined aquifer are variable and influence the overall water chemistry. The two primary water-quality concerns are concentrations of nitrate and iron. Local concentrations of these ions are directly related to oxidation and reduction (redox) reactions.

The relative intensity of redox potential of a solution is represented by Eh or pE ( $pE = 16.9Eh$ ). The redox potential is high (pE of approximately 13.8 based on the  $O_2/H_2O$  couple) as long as the water contains dissolved oxygen. After all the free oxygen has been consumed, pE is successively lowered through the processes of denitrification, reduction of manganese and iron species, sulfate reduction, and finally, fermentation. The approximate pE associated with several redox couples is given in Figure 6. Oxidation of organic matter usually accompanies reducing reactions.

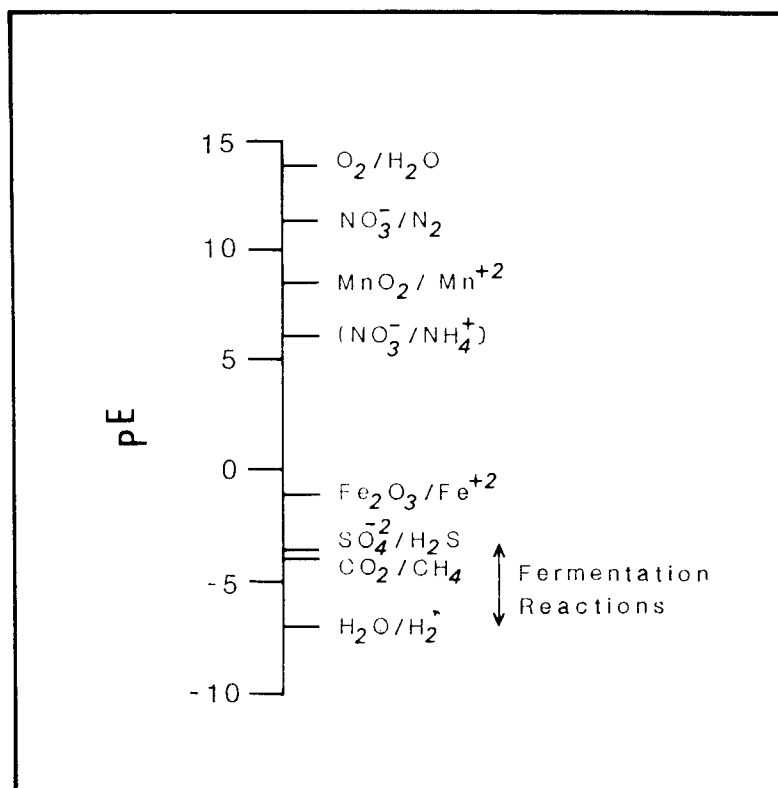


Figure 6. Approximate pE values at which various redox reactions occur in water at pH 7 and 25°C . (Modified after Drever, 1982, p. 281.)

TABLE 2. Average composition of precipitation from a station located in Lewes, Delaware, August 1978 to January 1983.

[Data provided by the MAP3S Precipitation Chemistry Network; mg/L, milligrams per liter; mmol/L, millimoles per liter]

Constituent	Concentration		3 x Concentration due to evaporation	
	mg/L	mmol/L	mg/L	mmol/L
Hydrogen, $H^+$	0.05	0.046	0.14	0.138
Sodium, $Na^+$	1.22	0.053	3.66	0.159
Ammonium, $NH_4^+$	0.23	0.013	0.69	0.039
Potassium, $K^+$	0.09	0.002	0.28	0.007
Calcium, $Ca^{+2}$	0.13	0.003	0.38	0.009
Magnesium, $Mg^{+2}$	0.13	0.005	0.38	0.016
Chloride, $Cl^-$	1.93	0.054	5.79	0.162
Sulfate, $SO_4^{-2}$	2.10	0.022	6.30	0.066
Nitrate, $NO_3^-$	1.23	0.020	3.69	0.060
Total	6.89	0.165	20.67	0.495

#### Soil Zone Reactions

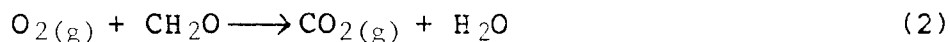
Leached of most of their soluble materials, the soils are strongly acidic and are generally low in plant nutrients (U.S. Department of Agriculture, 1974). The soil zone is still a strong influence on the chemistry of water in the unconfined aquifer, however, through the production of carbon dioxide ( $CO_2$ ) and the consumption of dissolved oxygen ( $O_2$ ).

Carbon dioxide is primarily produced by the oxidation of organic matter and the respiration of plant roots. Minor amounts of the total  $CO_2$  are generated by anaerobic reactions, such as reduction of sulfate or nitrate.

Carbon dioxide produced in the soil zone combines with water to form carbonic acid:



This acid is a reactant in silicate mineral dissolution and, therefore, a major weathering agent. Carbonic acid is also a reactant in the oxidation of nitrogen compounds in fertilizers and in the dissolution of carbonates. The rate and degree of consumption of dissolved oxygen depend on factors such as soil structure, porosity, permeability, frequency of recharge events, depth to water table, temperature, and nature and depth distribution of organic matter (Freeze and Cherry, 1979). Reduction may occur near land surface in poorly drained soils that have high organic content. All the oxygen may be consumed by oxidation of organic matter:



Dissolved oxygen not consumed by reactions with organic material in the soil zone moves into the ground-water system where it is consumed by oxidation of reduced species such as ferrous iron, ammonium, and sulfides. Organic deposits in deeper sediments also consume dissolved oxygen and reduce oxidized compounds such as sulfate.

### Sulfur Species

Natural sources of sulfur in the unconfined aquifer are atmospheric gases and organically bound sulfur. Sulfide and sulfate minerals have not been detected in the surficial sediments except for pyrite in a clay bed near Seaford (J. Talley, oral commun., 1986). Atmospheric sulfur consists primarily of sulfur compounds that originate from the combustion of fossil fuels. A smaller amount of sulfur originates in sea salt spray. About 6 mg/L of sulfate enters the aquifer via precipitation. The potential for reduction of atmospheric sulfate and the introduction of sulfur from organic decomposition varies with the amount of organic matter and redox conditions.

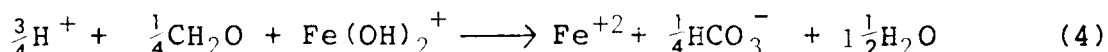
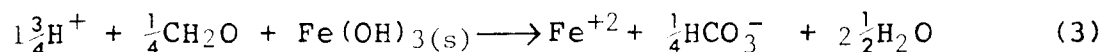
Most sulfur occurs as sulfate ( $\text{SO}_4^{-2}$ ) in the oxic parts of the aquifer. The reduction of sulfate is a slow process requiring bacterial action and sulfate and sulfide species can coexist in an aquifer under nonequilibrium conditions (Hem, 1970).

## Iron Oxides and Hydroxides

Dissolved iron is a common constituent in water where the unconfined aquifer is anoxic. Amorphous ferric hydroxide  $[\text{Fe}(\text{OH})_3]$  is the dominant form of iron where water contains dissolved oxygen. Equilibrium relationships studied by Hem and Cropper (1959) indicate that the behavior of ferric hydroxide is the chief control on the solubility of iron in water.

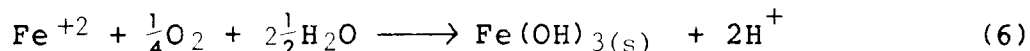
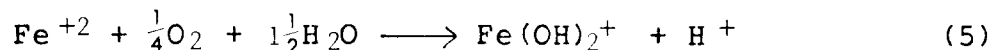
Solid and dissolved forms of iron in oxic water are in the ferric ( $\text{Fe}^{+3}$ ) state. Ferric hydroxide is precipitated and the small amount of iron remaining in solution is in the form of ferric ions including  $\text{Fe}^{+3}$ ,  $\text{FeOH}^{+2}$ ,  $\text{Fe}(\text{OH})_2^{+}$ .

The ferrous ( $\text{Fe}^{+2}$ ) ion predominates in reducing environments, and more iron can be in solution. In the reduction of iron and other inorganic constituents, some other constituent, usually organic matter, must be oxidized:



Thus, reduction of ferric iron produces bicarbonate and increases the alkalinity of the solution.

The reverse of these reduction reactions is the oxidation reaction where ferrous iron species come into contact with water containing dissolved oxygen:



Sand grains are frequently coated with ferric hydroxide in oxic parts of the aquifer. Layers of sand cemented by ferric oxide and hydroxide are also common in the unconfined aquifer, from near the surface to the base of the aquifer. These layers are often found at boundaries between layers with contrasting permeabilities within the aquifer. The most common occurrence, based on interpretation of well logs, is near the contact between the Columbia Formation and the underlying Chesapeake Group in areas where the Chesapeake Group is fine-grained. The abundance of these cemented layers is indicative that changes in redox potential within the ground-water system are common.

### Mineral Dissolution and Alteration

The major minerals in the sediments that react with ground water are feldspar, mica, aluminum silicate clay, and ferric-hydroxide coatings on the sand grains. Quartz, the most common mineral, is not significantly soluble under aquifer conditions. Heavy minerals are also present in small quantities and react with water, but their effect is probably insignificant to overall water chemistry.

#### Silicate Minerals

One of the most important weathering reactions is the incongruent dissolution of aluminum silicates which results in the structural breakdown of the primary aluminum silicate, the release of cations, and, usually, the formation of silicic acid ( $\text{H}_4\text{SiO}_4$ ). Also, alkalinity of ground water is increased and a solid residue that contains more aluminum than the original mineral is formed. Feldspars, principally orthoclase ( $\text{KAlSi}_3\text{O}_8$ ) and plagioclase ( $\text{Na}_{0.5}\text{Ca}_{0.5}\text{Al}_{1.5}\text{Si}_{2.8}\text{O}_8$ ), are the most abundant minerals available for reactions in the sediments of the unconfined aquifer. Kaolinite [ $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ ] is the main alteration product of these reactions. Other possible weathering products from feldspars are montmorillonite, vermiculite, illite, and gibbsite.

Incongruent dissolution of silicates is the primary source of sodium, potassium, calcium, bicarbonate, and silicic acid in water under natural conditions. In the dissolution of plagioclase, calcium ( $\text{Ca}^{+2}$ ) and sodium ( $\text{Na}^{+}$ ) are released to the water. Orthoclase feldspar is the major source of potassium ( $\text{K}^{+}$ ) ions. Magnesium ( $\text{Mg}^{+2}$ ) is contributed from weathering of micas and some heavy minerals.

Dissolved silica, represented as silicic acid,  $\text{H}_4\text{SiO}_4$ , is usually found in a non-ionic form that does not react with other ions in water. Its concentration can be affected by reactions with certain clay minerals. The concentration of dissolved silica is indicative of the degree of dissolution of silicate minerals and alteration of the residual weathering products resulting from contact with water.

Variations in weathering intensity result in different degrees of leaching cations and silicic acid from the original minerals. In general, kaolinite and oxides of iron and aluminum are solid products of intense weathering. Hydrous mica, vermiculite, and montmorillonite are the products of less intense weathering and may be further altered as weathering continues.



## Clay Minerals and Cation Exchange

The assemblage of clay minerals in southwestern Delaware is dominated by kaolinite, illite, and vermiculite in the soil zone and the upper part of the aquifer (Pickett, 1970). Clays in the deeper sediments are composed of kaolinite, illite, and montmorillonite in varying proportions (Hess, 1977).

Cation exchange reactions with clay minerals can modify water chemistry. The significance of these reactions varies with the type and the amount of clay minerals present and the concentration of cations in solution.

Surface areas of clay particles are typically large. Most clay particles carry net negative charges that attract cations to the particle surfaces and create an "ionic double layer." The strength of the bonds holding the adsorbed cations are affected by changes in pH. In acidic soils,  $H^+$  is preferentially retained on exchange sites and  $Ca^{+2}$ ,  $Mg^{+2}$ ,  $K^+$ , and  $Na^+$  are released into solution and carried away by infiltrating ground water. Where pH is equal to or greater than 6,  $H^+$  is loosely held and  $Ca^{+2}$  and  $Mg^{+2}$  are dominant on the exchange sites.

Variations in the crystal structures of the clays result in different capacities for cation exchange. Vermiculite and montmorillonite have the highest cation exchange capacities of the clays present in the study area. These minerals have a high net negative charge as the result of attraction of water molecules between the crystal units that cause expansion and expose a large internal surface. Illite is a nonexpanding mineral whose cation exchange capacity is less than that of vermiculite and montmorillonite. Potassium ions are strongly attracted to illite and are fixed at the cation exchange sites between the crystal layers. Because the lattice of kaolinite is fixed, cations are attracted only to its outer surface. Its capacity to adsorb cations is one of the lowest of the silicate clay minerals.

As weathering proceeds in humid regions, the displacement of cations by aluminum and hydrogen ions produces aluminum hydroxide clays, including kaolinite, whereas the more soluble ions are removed by leaching. The decomposition of kaolinite can result in the formation of insoluble aluminum oxides such as gibbsite. Gibbsite may also form in place of kaolinite if dissolved silica produced in the weathering reactions is leached rapidly from its source area. Iron oxides such as limonite and goethite are commonly associated with gibbsite and represent the most intense stage of weathering. Hydrous oxide clays are intermixed with silicate clays in the sediments of the unconfined aquifer.

In a study of weathering profiles in the sediments of selected Coastal Plain Formations, Owens and others (1983), discussed the clay mineralogy of the Beaverdam Sand and Pensauken Formation (Beaverdam and Columbia formations, respectively, of this report) at a site east of the study area. They defined at least two weathering cycles in these units. The first cycle produced a predominantly kaolinite-gibbsite-goethite assemblage representing intense leaching of the sediments. The second cycle produced a vermiculite-illite-amorphous iron oxide(?) assemblage in the upper beds, but had little effect in the underlying sediments. These assemblages are probably analogous to weathering profiles in southwest Delaware where the sediments and the climate are similar to those of the Owens and others (1983) study area.

#### ANTHROPOGENIC INFLUENCES ON WATER CHEMISTRY

Ions leached from fertilizer, solid waste, and sewage applied on or near the land surface can have a significant effect on the chemistry of the water in the unconfined aquifer. This is because the natural water has a low dissolved-solids concentration, the water table is close to the land surface, and most of the surficial sediments are permeable.

Crop production is the most widespread land use. Livestock production (primarily poultry) and the use of domestic septic systems are also widespread, but the land area directly affected by these uses is much smaller than that affected by crop production.

#### Land Use

##### Agricultural Influence

The principal agricultural practices that influence water chemistry are applications of inorganic fertilizer, manure, and lime for improving crop production. Manure and inorganic fertilizer contain nitrogen. Other components of inorganic fertilizer necessary for plant growth that may affect quality of ground water are potassium and phosphorus. Fertilizer may also contain sulfate and micronutrients which include small amounts of iron, manganese, zinc, boron, copper, chlorine, cobalt, and molybdenum (Brady, 1974). These micronutrients are used by plants in small quantities but the amounts present probably do not significantly influence water quality.

Nitrogen

Most of the nitrogen applied as inorganic fertilizer is in ammonium compounds. Nitrogen from manure and from effluent of septic systems is in the form of ammonium and organic nitrogen compounds.

Manure is applied to fields to supply all or part of nitrogen requirements for crops. Poultry manure, the most common type used in Delaware, also contains significant quantities of the other major nutrients (Table 3).

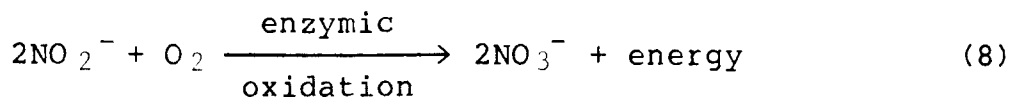
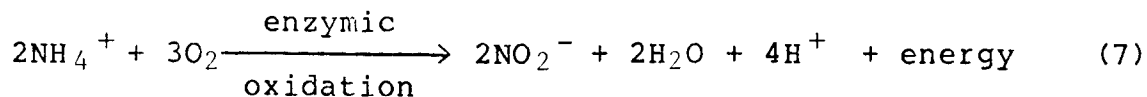
Ground water can also be influenced by constituents leached from manure stockpiles and from areas where animals are confined. Concentrations of chemicals from these sources differ from those leached from manure applied on fields because the components are not used by crops and are concentrated in small areas. In addition, such constituents are not combined with those from lime and inorganic fertilizer.

TABLE 3. Major chemical components in poultry manure and sewage effluent.

[Data of poultry manure, from Overcash, Humenik, and Miner, 1983, p. 147-180; data of sewage effluent, from LeBlanc, 1982, p. 7]

Component	Poultry manure (millimoles per liter)	Sewage effluent (millimoles per liter)
Calcium	773	0.30
Magnesium	176	0.18
Sodium	132	2.26
Potassium	306	0.30
Chloride	170	0.93
Nitrogen, total	2499	1.36
Sulfur	140	0.39
Phosphorus, total	387	0.06

Organic and ammonium nitrogen ( $\text{NH}_4^+$ ) are usually converted to nitrate ( $\text{NO}_3^-$ ) in the soil zone where organic matter and oxygen are abundant. Organic nitrogen is first converted to ammonium through the ammonification process. Then ammonium is oxidized to nitrate in the presence of nitrifying bacteria. This two-step process is called nitrification and proceeds:



The oxidation of nitrite to nitrate is rapid and nitrate is the stable oxidized form of dissolved nitrogen in ground water. Nitrification is an acidifying process; the hydrogen ions produced by this process can lower the pH of the solution if the system is not buffered.

Nitrification depends on several factors because nitrifying bacteria are sensitive to their environment. The rate and degree of nitrification and, therefore, the amount and form of nitrogen entering the ground water are related to variations in aeration, temperature, moisture, availability of exchangeable ions, fertilizers, and the ratio of carbon to nitrogen. Nitrate can be reduced to nitrous oxide or nitrogen gas in reducing environments by the process of denitrification.

The amounts of nitrate and other nitrogen species in natural water vary with differences in the organic content of the soil and redox conditions. In well-drained soils containing little organic matter, the source of naturally occurring nitrate is almost exclusively atmospheric precipitation.

Nitrification does not occur in areas where soils are poorly drained and dissolved oxygen concentration of the water is zero. Ammonium and organic nitrogen are the forms of nitrogen in water. Ammonium and potassium ions are preferentially adsorbed on interlayer exchange sites of certain clay minerals. Vermiculite has the greatest affinity for both ions; however, illite also fixes ammonium. Ammonium and potassium ions are readily exchanged for other interlayer cations; however, once they are fixed they are not likely to be removed.

Regardless of the source, reactions of nitrogen species in water are the same under similar aquifer conditions. Comparison of nitrate concentrations in water to the concentrations of other ions and to ratios of nitrogen isotopes can help identify the source of the nitrogen.

### Potassium

The potassium compound applied to fields to increase the amount of potassium ion available for crops is usually potassium chloride, KCl.

Potassium content in most soils is high, but more than 90 percent of the potassium is in relatively unavailable forms such as feldspars and micas, which are resistant to weathering (Brady, 1974), or are fixed on interlayer exchange sites in illite and vermiculite. Potassium available for plant growth is found in the pore water of soils where it is subject to leaching, and on certain exchange sites of colloidal surfaces.

### Phosphorus

Phosphorus, usually expressed as phosphorus pentoxide ( $P_2O_5$ ) in fertilizer, is a potential source of phosphate in water. Phosphorus is also a product of animal metabolic wastes and, therefore, a component of sewage and manure. Only trace amounts of phosphate-bearing minerals have been noted in Delaware (Jordan, 1964). Phosphate is rarely found in local ground water because phosphate ions form complexes with many other ions in solution in water. Phosphate is also fixed by silicate clays and hydrous oxides of iron, aluminum, and manganese.

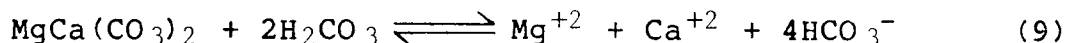
### Sulfur

Sulfur is sometimes added to the soil as gypsum ( $CaSO_4 \cdot 2H_2O$ ) or as a sulfate component in fertilizer. Sulfate is not a common fertilizer component in the study area because adequate sulfur is usually supplied by precipitation and organic decomposition. Sulfate ions can be retained in acidic soils whose contents of kaolinite and hydrous iron and aluminum oxides are high. An increase in pH (as from liming) will tend to release the adsorbed sulfate (Brady 1974).

Lime

The application of lime in the form of oxides and hydroxides of calcium and magnesium or ground limestone, calcite, and dolomite buffers the acidity caused by nitrification. It also enhances the availability and uptake by plants of other elements such as calcium, magnesium, molybdenum, and phosphorus and reduces the solubility of iron, aluminum, and manganese, which can be toxic to plants. Dolomite in crushed form is the most common carbonate used in Delaware.

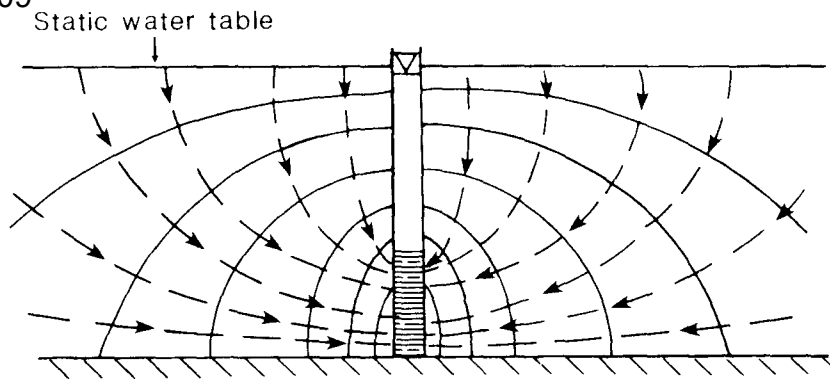
All forms of lime react on contact with atmospheric carbon dioxide to produce bicarbonate. Calcium and magnesium carbonates are readily dissolved to ionic calcium, magnesium, and bicarbonate:

Septic-System Effluent

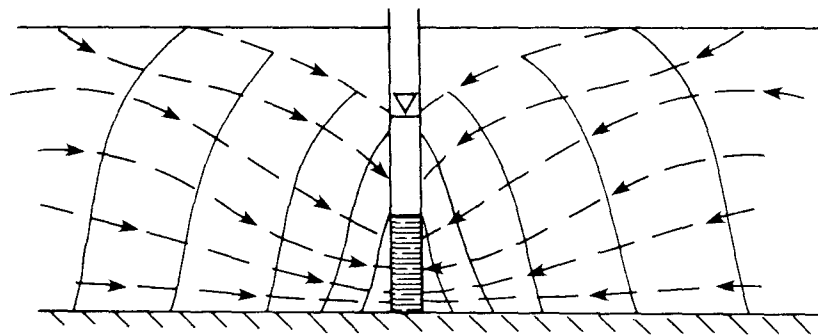
The effluent from domestic septic systems is discharged into tile fields or seepage beds buried in or just below the subsoil. Therefore, it is not directly involved in reactions in the soil zone or the uptake by plants. The major components of septic-tank effluent are similar to those in poultry manure, but the proportions in each are different (Table 3). These differences result in comparable variations in water chemistry. Aquifer water chemistry is not significantly influenced by isolated septic systems, except immediately downgradient from the system, because of dilution and retardation due to adsorption of ions. The effects on water chemistry can be locally significant in residential areas containing closely spaced septic systems.

Ground-Water Withdrawals

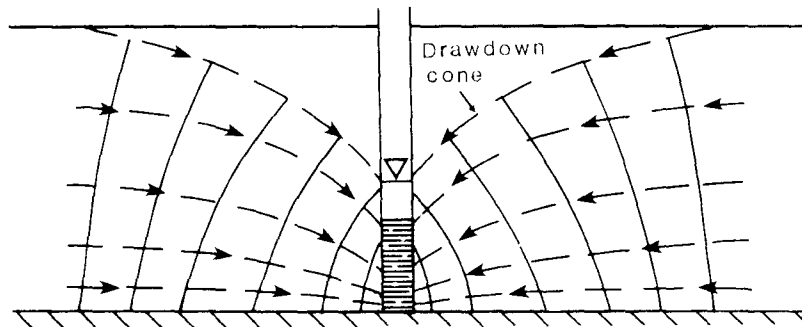
Most of the wells in the unconfined aquifer are pumped intermittently, which does not allow the ground-water flow system to reach steady state. In the early stages of pumping a well in an unconfined aquifer, there is a large vertical component of flow from the water table to the screen (Figure 7A). This allows water that was influenced by local land use and soil type surrounding the well to be drawn toward the screened interval. The horizontal component of flow does not become significant until the system approaches steady state. Because of the short, intermittent pumping periods, the initial and intermediate stages of pumping shown in Figure 7 (A and B) are probably most characteristic of flow to wells.



- A. Initial stage in pumping an unconfined aquifer. Most water follows a path with a high vertical component from the water table to the screen.



- B. Intermediate stage in pumping an unconfined aquifer. Radial component of flow becomes more pronounced but contribution from drawdown cone in immediate vicinity of well is still important.



- C. Approximate steady state stage in pumping an unconfined aquifer. Profile of cone of depression is established. Nearly all water originating near outer edge of area of influence and stable primarily radial flow pattern established.

Flow lines → —

Equipotential lines ———

Figure 7. Development of flow distribution around a discharging well in an unconfined aquifer. (Modified from U.S. Department of the Interior, 1981, p. 45.)

Irrigation wells probably affect the aquifer more than other wells in the area because of their high pumping rates, and, therefore, the flow system around these wells should be considered in some detail. Johnston (1973) gives an example of the extent of expansion of the cone of depression around a well pumping at 500 gallons per minute (gal/min), which is a reasonable pumping rate for an irrigation well in the surficial deposits. For a transmissivity of 7,000 ft<sup>2</sup>/d and a specific yield of 0.15, the calculated cone of depression would extend about 600 feet from the well after 1 day of pumping.

In most of the areas under irrigation, the actual transmissivity of the unconfined aquifer is probably greater than 7,000 ft<sup>2</sup>/d. Transmissivities ranged from 9,200 to 13,000 ft<sup>2</sup>/d for three pump tests in the southern part of the study area (Johnston 1973). Johnston (1977) found the average transmissivity of the aquifer to be 9,500 ft<sup>2</sup>/d in an area adjacent to the study area after final calibration of a ground-water flow model.

The hydraulic gradient in western Sussex County generally ranges from about 3 to 10 feet/mile (ft/mi) (Sundstrom and Pickett 1970). The calculated particle velocity of ground-water movement ranges from 0.36 to 1.2 (ft/d). During the irrigation season (from June to September), the water that recharged the aquifer within the area of influence of the pumping well is virtually recycled through the system, except for minor amounts which have moved outside the area of influence when the well was not pumping. During the remaining 8 months of the year, on the basis of the calculated velocities, the ground water potentially affected by irrigation pumpage can move between 90 and 300 feet downgradient from the well. Some of the water influenced by irrigation pumpage during 1 year will still be within the area of influence of the well during the next irrigation season. The water outside of the area of influence will be mixed with other water in the flow system. The recycling of water in the area of influence of the well could benefit crop production because the water-soluble nutrients that are leached into the ground water are made available to plants again through irrigation.

Chemical evidence for mixing of components leached from the land surface into deeper parts of the aquifer is shown by a comparison of nitrate concentrations in wells with short screened intervals to wells with long screened intervals (Figure 8). The six highest nitrate concentrations in wells with shorter screened intervals (20 feet or less) were in wells less than 50 feet deep. Nitrate concentrations in wells with screened intervals of 20 feet or less decreased with depth in wells greater than 50 feet deep. A similar pattern was seen by Ritter and



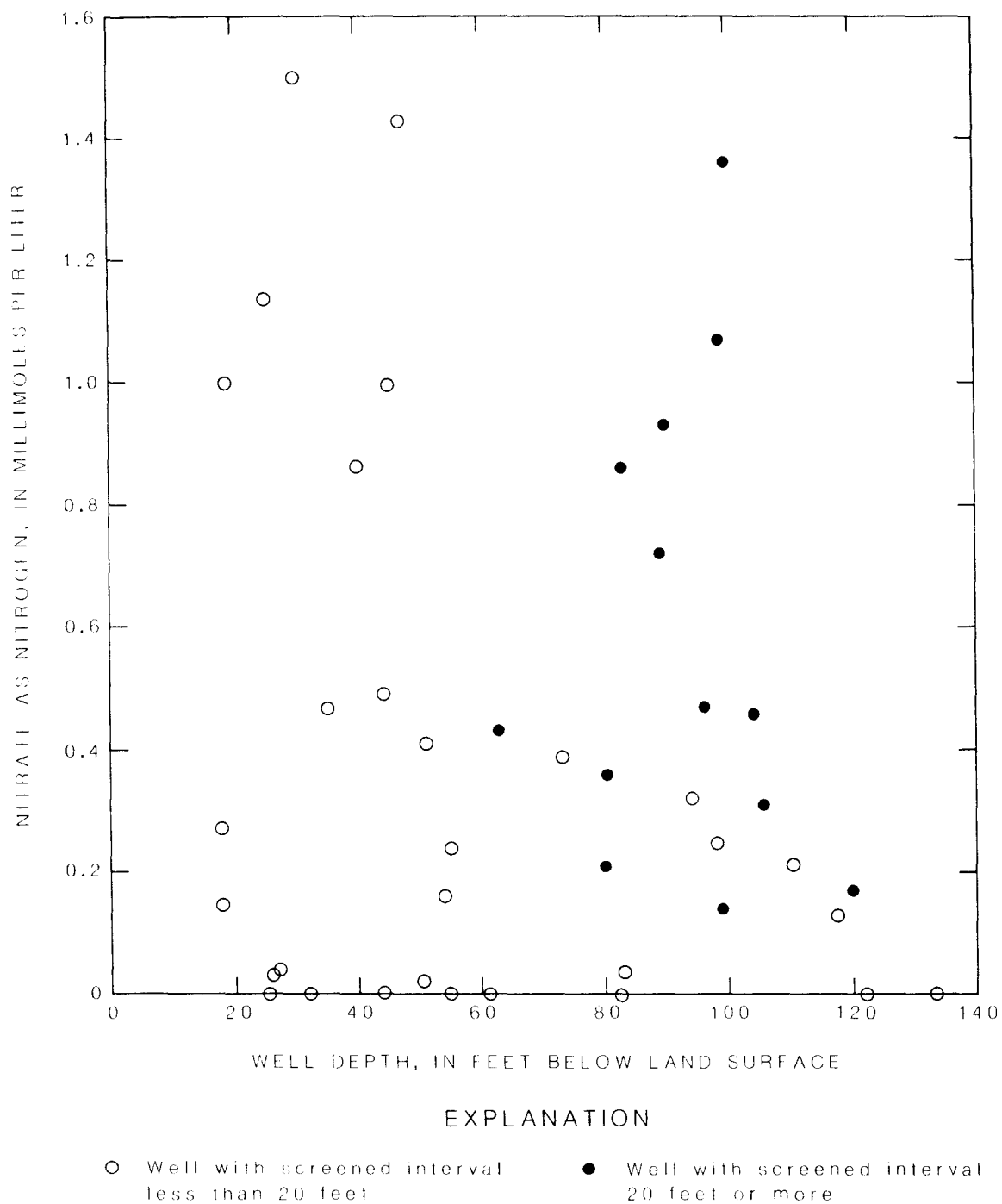


Figure 8. Relation of nitrate concentration to well depth for water in the unconfined aquifer.

Chirnside (1982). They found the highest median and average nitrate concentrations in wells as deep as 40 feet and a decrease in nitrate with increasing depth over 40 feet. These trends are an indication that nitrate concentrations leached into the natural flow system decrease with depth because of dilution with water in deeper parts of the system.

Nitrate concentrations in water from wells with screened intervals of more than 20 feet do not decrease at depths greater than 50 feet (Figure 8). These wells are primarily irrigation wells in well- or excessively well-drained soils where fertilizer components are readily leached into the aquifer. Nitrate concentrations exceeding 10 mg/L as nitrogen (0.72 millimoles per liter, mmol/L) are found in water from wells as deep as 100 feet. Nitrate is apparently moved into the deeper parts of the aquifer by pumping of these wells. In a study of nitrate distribution in ground water in Redlands, Calif., Eccles and Bradford (1977) also found that pumping can cause high concentrations of nitrate near the water table to be moved deeper into the aquifer around the well.

## GEOCHEMISTRY OF WATER IN THE UNCONFINED AQUIFER

### Natural Ground Water

The major constituents in the water of the unconfined aquifer are a complex combination of ions from natural sources, modified by additions resulting from variations in land use. Chloride, from precipitation, is the only major component in water that is not involved in reactions with other ions or adsorbed on mineral surfaces. Therefore, chloride concentrations near or below that of concentrated precipitation (5.8 mg/L, Table 2) are considered an indicator of natural conditions in ground water.

Nitrate ions in oxic water are stable, and, therefore, nitrate concentrations near or less than 3.7 mg/L as nitrogen, which is the average amount resulting from concentrated precipitation, are probably the maximum that could be expected under natural conditions. However, nitrate and ammonium nitrogen are readily available for uptake by plants, which probably reduces the concentrations of nitrate entering ground water from precipitation.

Analyses of water in the unconfined aquifer (from wells with natural or virtually natural water chemistry) are shown in Table 4. Some of these wells contain water in a reducing (anoxic)

Table 4. Chemical analyses of water from wells in the unconfined aquifer with natural or nearly natural water chemistry

[Date sampled: month-day-year; Screened interval: in feet below land surface; Bicarbonate: calculated from field alkalinity; Results shown in milligrams per liter except for pH or as noted].

Well no.	Date sampled	Screened interval	Specific conductance ( $\mu\text{S}/\text{cm}$ at $25^\circ\text{C}$ )	pH	Dissolved oxygen	Silica	Iron, total	Calcium	Magnesium	Sodium	Potassium	Nitrate+ nitrite nitrogen	Ammonia as nitrogen	Chloride	Bicarbonate	Sulfate
Jb31-1	6- 9-83	22-27	90	5.6	2.2	20	0.76	9.5	1.6	5.1	1.2	0.61	<0.01	4.0	25.6	19.0
Mc31-3	9-11-83	41-61	132	6.3	0.0	23	5.6	12.0	2.1	6.2	1.2	0.19	0.13	5.8	52.4	15.0
Md55-2	9- 9-83	? -50	40	5.8	3.4	30	0.04	2.0	0.22	5.4	0.4	0.23	<0.01	4.2	15.6	0.6
Nd25-3	10-18-83	117-122	72	6.4	0.4	34	2.6	2.6	0.64	10.0	1.0	<0.10	0.18	4.5	39.0	1.3
Nd25-4	10-14-83	85-90	47	6.4	0.1	35	4.3	0.59	0.17	7.1	0.5	<0.10	0.03	5.9	21.9	1.8
Nd25-5	10-18-83	49-54	56	5.9	3.6	23	0.02	2.5	0.45	7.2	0.9	2.3	<0.01	4.7	12.2	0.4
Nd25-6	10-18-83	39-44	49	5.8	2.3	23	0.01	2.3	0.36	6.7	0.8	0.03	0.03	4.4	15.9	0.4
Ne54-3	3-14-83	72-82	39	5.6	2.6	14	0.3	1.2	0.35	4.4	1.2	<0.10	<0.01	5.0	12.0	0.9
Of41-1	2- 9-83	97-117	59	6.0	8.5	28	0.7	2.8	0.59	6.7	1.3	1.8	<0.01	5.8	18.0	<5.0
Qc52-6	9- 8-83	60-120	43	5.4	3.1	16	<0.003	2.6	0.9	4.8	1.6	2.4	0.02	6.0	5.8	2.0

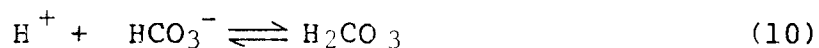
environment. Anoxic conditions are defined in this report as water that has 0.4 mg/L or less dissolved oxygen.

Most of the remaining major dissolved constituents of ground water are derived from atmospheric precipitation and weathering of silicate minerals. Sodium is the major cation from both sources. The source of sodium in precipitation is sea salt, and the concentration of sodium in precipitation is similar to that of chloride (Table 2). Other constituents dissolved in precipitation are calcium, potassium, and magnesium ions (Table 2). Magnesium concentrations could be accounted for solely through input from precipitation in many wells sampled.

Sodium and calcium concentrations in water are usually higher than potassium concentrations because plagioclase is more soluble than orthoclase. Concentrations of cations are also affected by ion exchange reactions. Divalent calcium and magnesium ions are preferentially retained on exchange sites over monovalent sodium; potassium ions can be fixed in the lattice of certain illitic clays.

In water from wells Jb31-1 and Mc31-3, calcium concentrations are greater than those of sodium. On the basis of geologic data, these wells may be screened in Chesapeake Group sediments. Dissolution of shell material (calcium carbonate) may cause the higher calcium concentrations.

Bicarbonate,  $\text{HCO}_3^-$ , is the major anion in natural water of the unconfined aquifer and is the only anion resulting from mineral dissolution. Bicarbonate concentration should increase as mineral dissolution continues, but the concentration is also affected by reactions such as nitrification that increase hydrogen ion activity. Bicarbonate concentrations are depleted by reacting with hydrogen ions to form carbonic acid:



This reaction will buffer the pH of the solution as long as some bicarbonate remains. When available bicarbonate is consumed, the pH of the solution will drop.

Redox reactions are also an important control on concentrations of certain constituents in natural water, notably iron, sulfur, and bicarbonate. Water in a reducing environment is frequently characterized by high concentrations of bicarbonate and iron because of the reduction of ferric hydroxide, (Reactions 3 and 4, p. 22). Reduction of sulfate to hydrogen sulfide gas also produces bicarbonate. In oxic water, sulfate ions may be

retained in acidic soils. Both of these processes result in lower sulfate concentrations.

Because the unconfined aquifer is composed primarily of insoluble quartz sand, the concentration of dissolved solids in the water is generally low. The specific conductance of oxic water samples ranged from 39 to 90  $\mu\text{S}/\text{cm}$  (microsiemens per centimeter at 25°C, formerly micromhos per centimeter at 25°C) and that of anoxic water samples ranged from 47 to 132  $\mu\text{S}/\text{cm}$  (Table 4). The generally high permeabilities of the sediments also reduce contact time for reactions between water and aquifer materials to occur.

#### Relation of Land Use and Soils to Ground-Water Chemistry

Land use and its effect on ground water is usually related to soil characteristics of the area. For example, poorly drained soils are not well suited for agriculture and, as a result, are usually wooded. On excessively drained soils, irrigation and large amounts of fertilizer are necessary for crop production because of the low moisture capacity and the low natural fertility of the soil. These variations affect both the type of land use and the quantity of applied constituents that may leach into the water.

Variations in the chemical composition of components associated with different land uses should result in comparable variations in the water chemistry. These variations should be apparent in water with higher concentrations of ions leached from surficial sources when contrasted against naturally occurring water that contains a lower concentration of ions.

#### Nitrogen

Nitrate concentration is used as an indicator of the effects of land use because it is a common constituent in agricultural fertilizers and domestic effluent. Nitrate is stable in an oxidizing environment and is found naturally only in low concentrations in the unconfined aquifer.

The relation of nitrate concentration to other ion concentrations is shown in Figures 9 to 13. The most apparent correlations in these graphs seem to be related to agricultural practices. Crop production is the major land use and many of the wells sampled were pumped for irrigation and other agricultural uses, or were adjacent to cultivated areas.

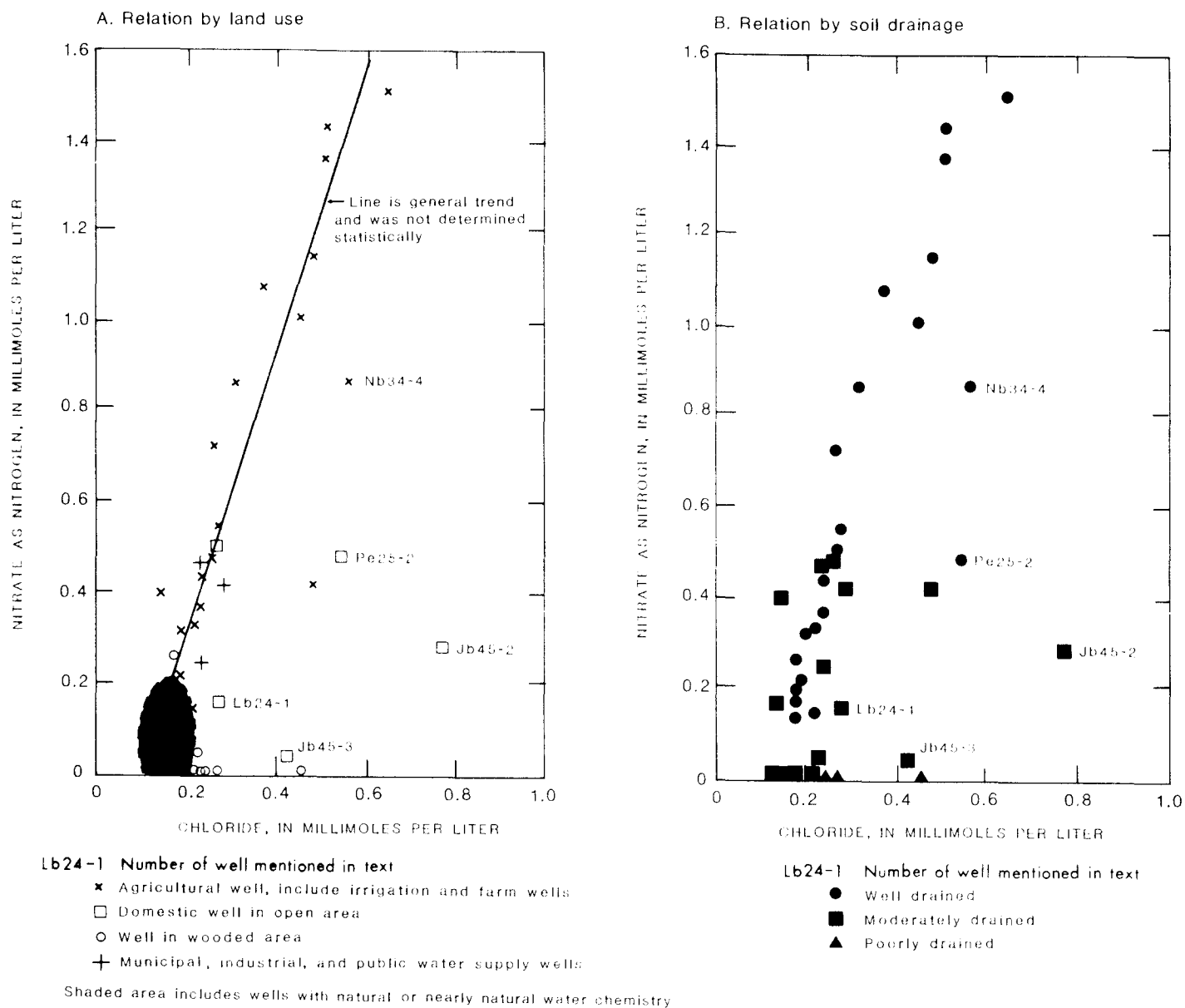


Figure 9. Relation of nitrate concentration to chloride concentration for water in the unconfined aquifer.

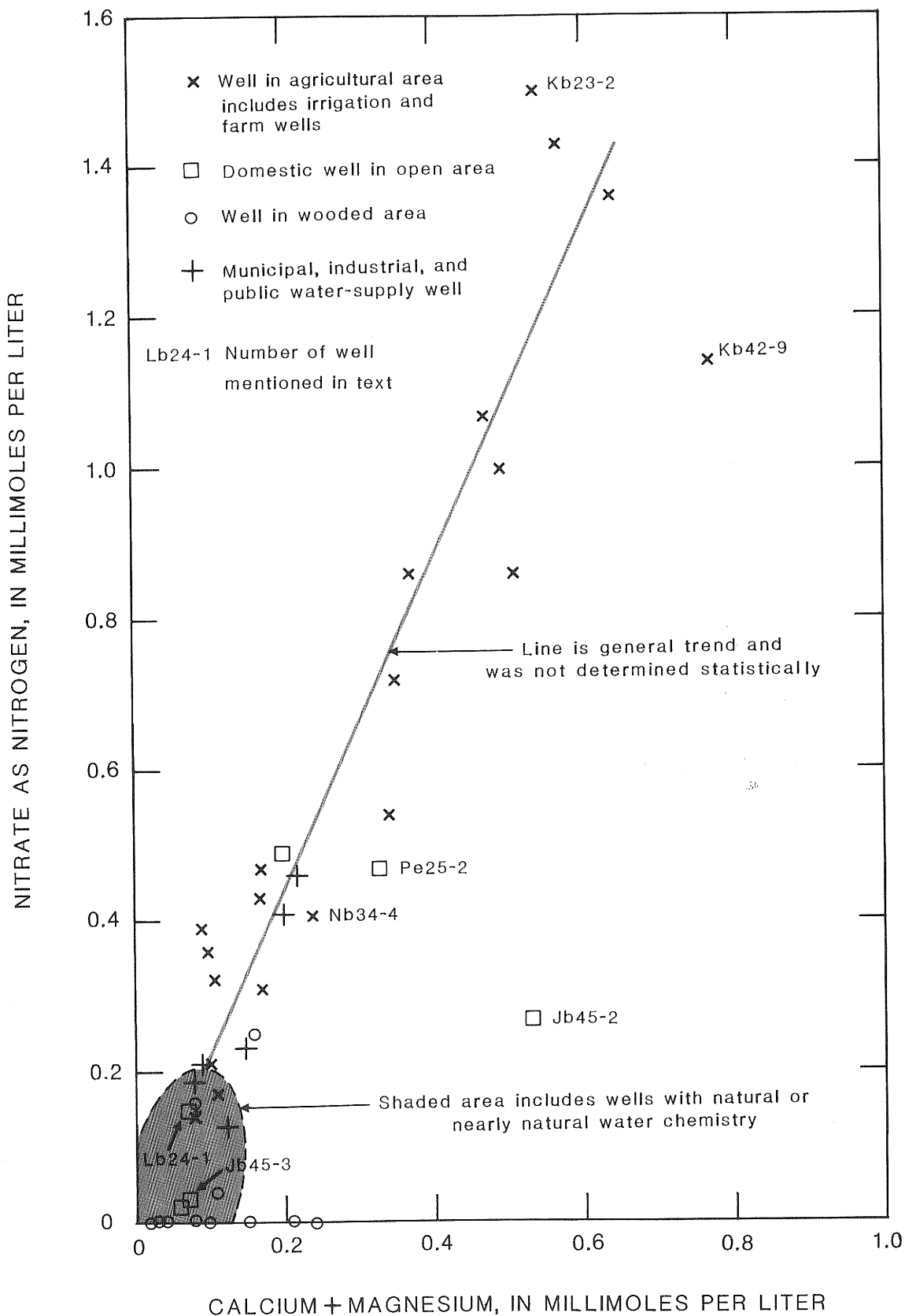


Figure 10. Relation of nitrate concentration to calcium plus magnesium concentration for water in the unconfined aquifer.

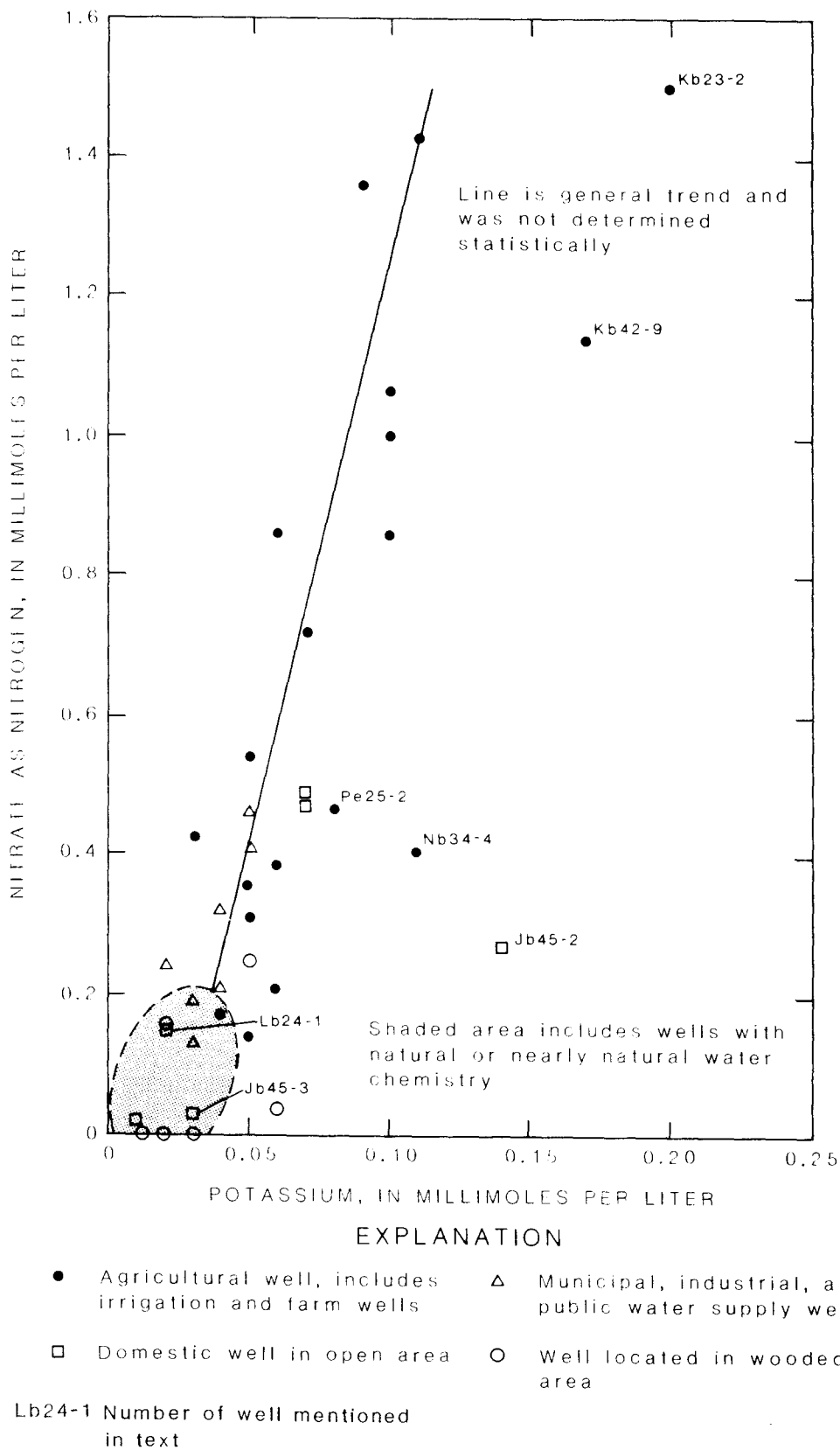
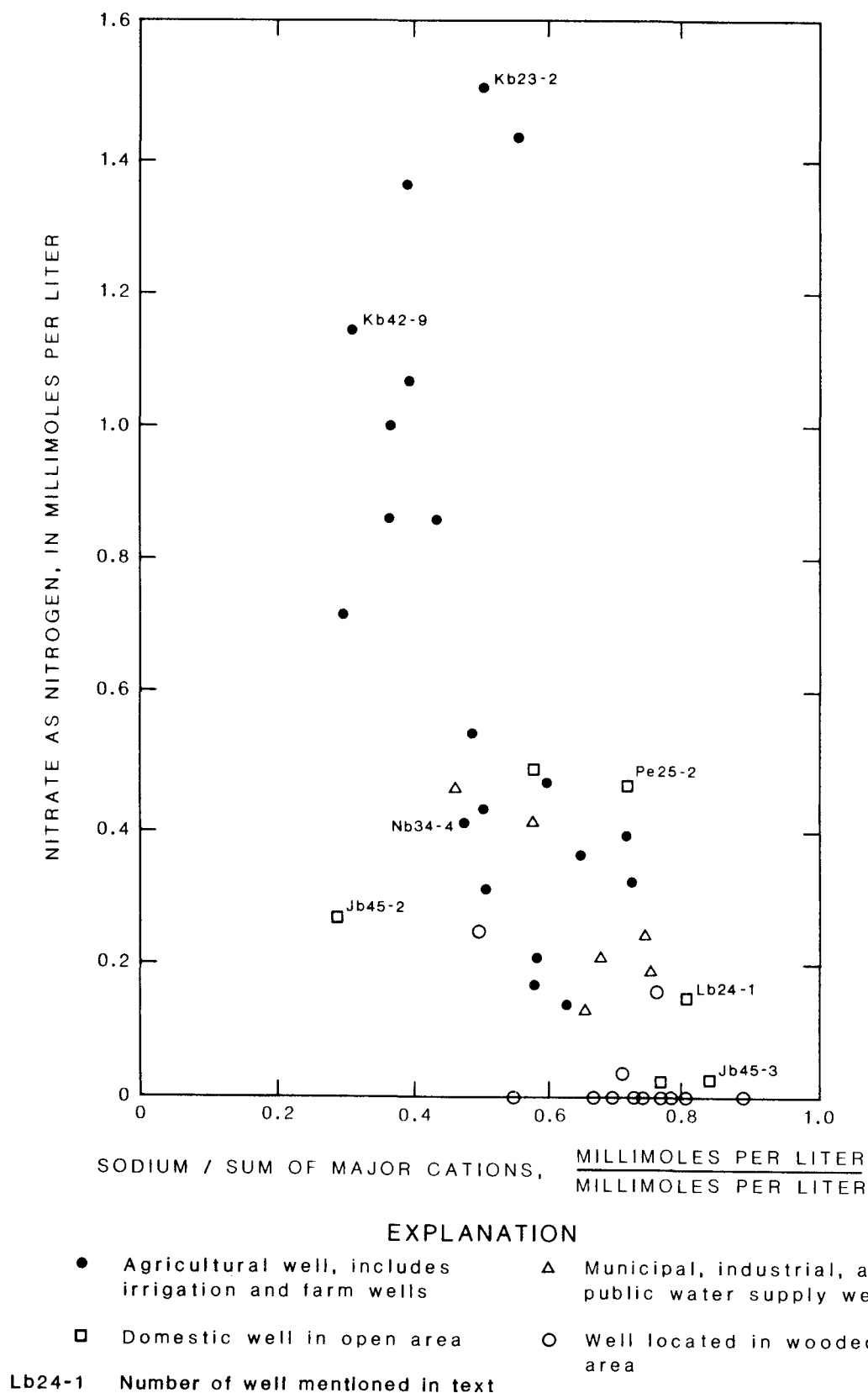


Figure 11. Relation of nitrate concentration to potassium concentration for water in the unconfined aquifer.





**Figure 12. Relation of nitrate concentration to the ratio of concentration of sodium to the sum of major cations for water in the unconfined aquifer.**

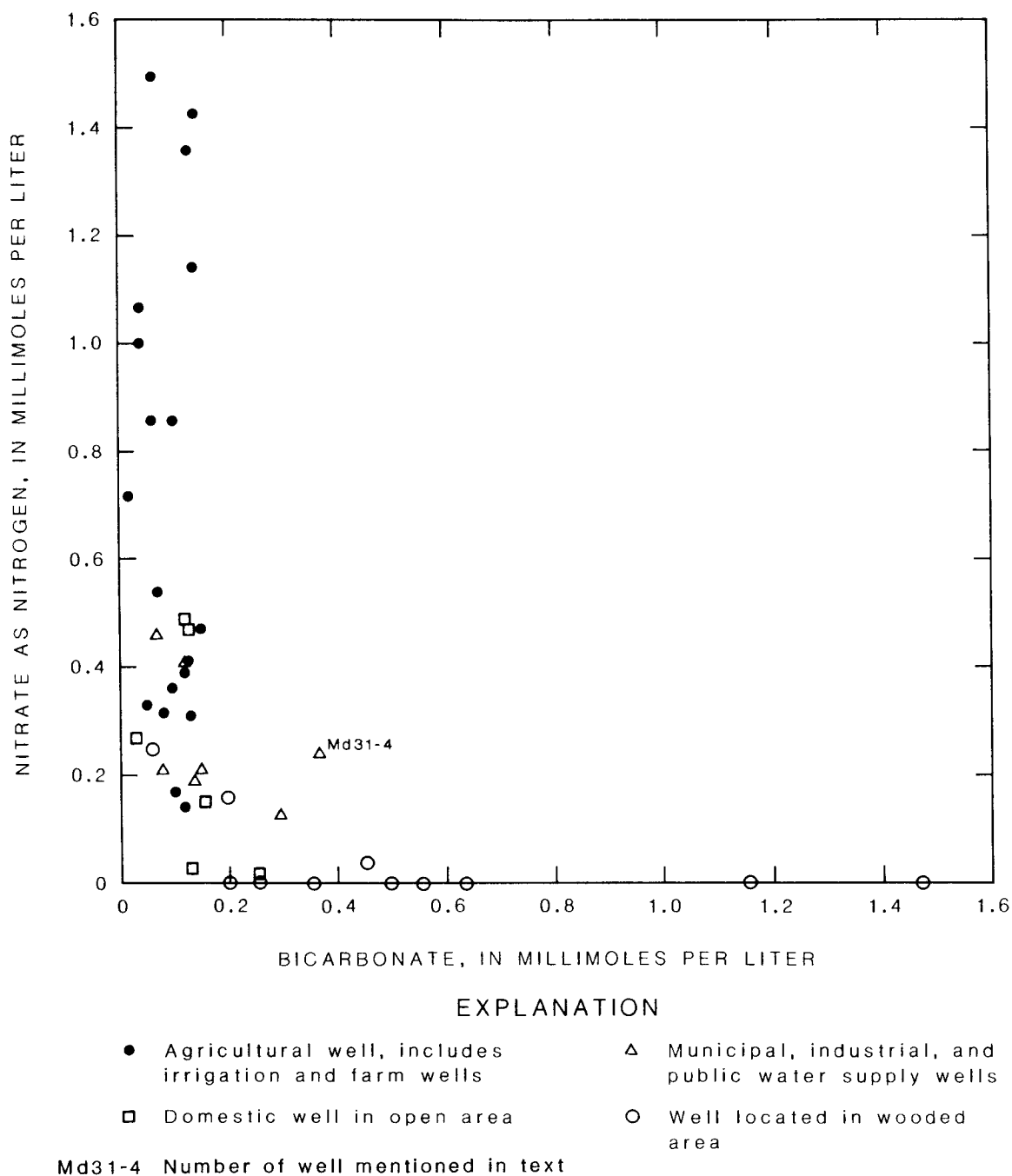


Figure 13. Relation of nitrate concentration to bicarbonate concentration for water in the unconfined aquifer.

There is a generally linear correlation between chloride and nitrate concentrations in most of the agricultural wells (Figure 9A) and several public and domestic wells that are located adjacent to agricultural areas. This correlation is probably due to proportional application rates of nitrogen fertilizers (inorganic and manure) to potassium chloride. Most of the nitrogen applied to cropland is in the form of organic matter and ammonium compounds, and, because the nitrification process is acidifying, certain amounts of cations (from agricultural dolomite,  $\text{CaMg}(\text{CO}_3)_2$ ) must be applied to maintain a soil pH near 5.6, the optimum pH for crop production. This conclusion is supported by the linear relation between calcium plus magnesium and nitrate concentrations in Figure 10, and nitrate and chloride concentrations in Figure 9.

Potassium chloride is commonly applied as a supplement to nitrogen-based fertilizers. There should be a linear correlation between potassium and nitrate concentrations similar to that between chloride and nitrate concentrations, but the correlation should be proportionately different from that for chloride and nitrate. This is illustrated in Figure 11. Concentrations of potassium and chloride are lower in water in wooded areas than elsewhere. Ground water in wells in wooded areas appears to be unaffected by agricultural practices.

Because chloride concentrations are usually related to nitrate concentrations in agricultural wells, chloride should be related to other ions that show a similar relation to nitrate. A plot of chloride against potassium concentrations (Figure 14) shows a direct correlation for most agricultural wells, probably owing to application of potassium chloride to the land.

Soil permeability also seems to affect water chemistry. The highest nitrate concentration of a moderately well-drained soil in this study is 0.47 mmol/L or 6.5 mg/L as nitrogen (Figure 9B). Most high nitrate concentrations are associated with agricultural wells in soils that are well- or excessively well-drained. Chemicals applied to the land are readily leached from these soils. Thus, greater amounts of nitrogen fertilizer must be applied to the soils to maintain concentrations of nitrogen in the soil zone appropriate for crop production. Irrigation of well- and excessively well-drained soils promotes leaching of fertilizer components and, as a result, nitrate concentrations may be high in water from irrigation wells.

Plots of several concentrations of nitrate and chloride (Figure 9) are to the right of the generalized line of correlation. This condition could be caused by variations in either land use or redox potential of the water, or both. Four of the

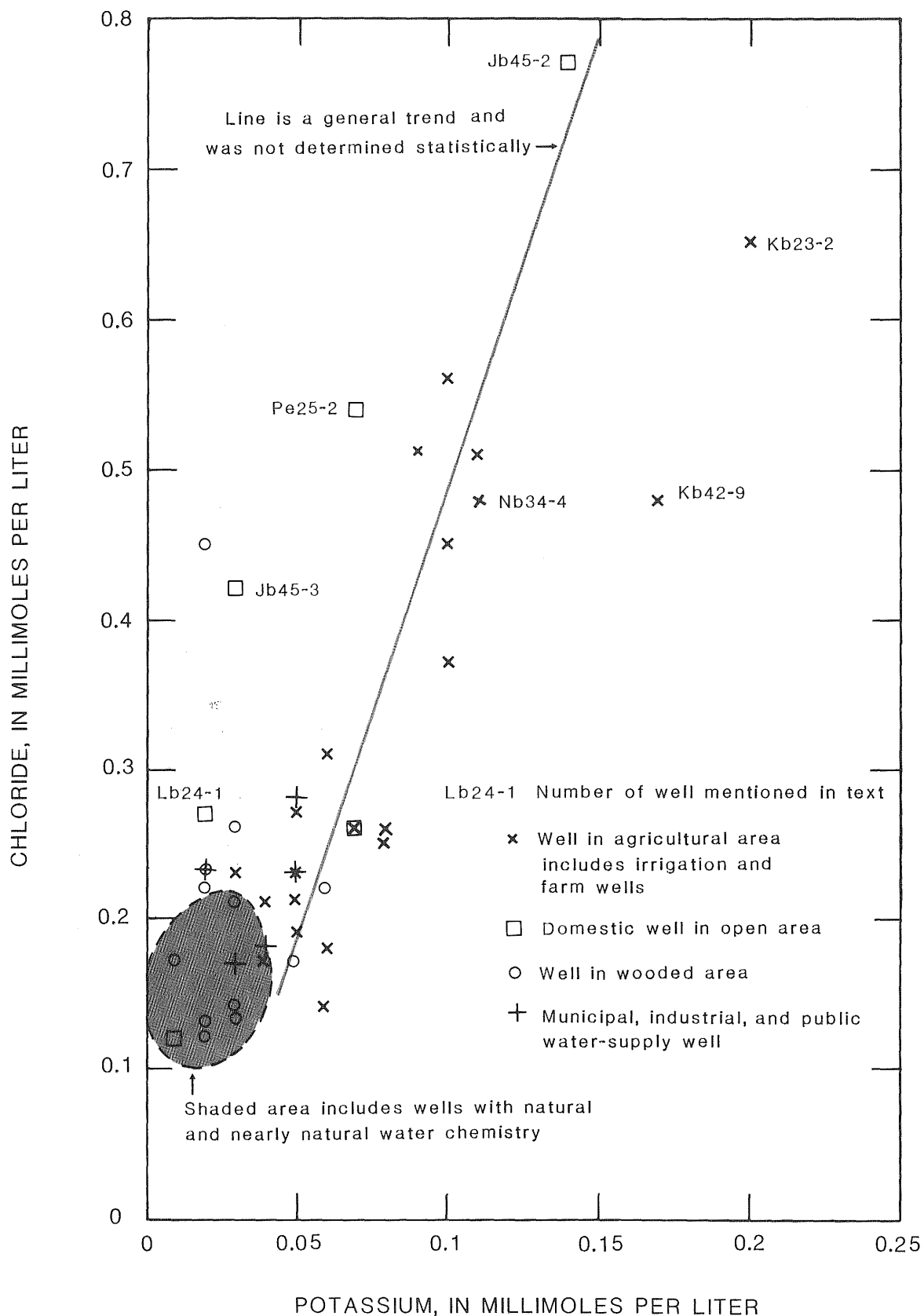


Figure 14. Relation of chloride concentration to potassium concentration for water in the unconfined aquifer.

wells, Jb45-2, Jb45-3, Lb24-1, and Pe25-2, are domestic wells in predominantly agricultural areas. The concentration of dissolved iron (2.4 mg/L) in water from well Jb45-3, is an indication that the oxidized form of nitrogen, which is nitrate, is probably unstable. Concentrations of dissolved iron in water from the other three wells exceed 0.1 mg/L. These iron concentrations and low nitrate concentrations may be due to the reducing environment in the wells. The low concentration of nitrate in well Jb45-2, in particular, seems to be the result of reducing conditions.

There is no increase in the concentrations of calcium, magnesium, and potassium ions relative to nitrate ion in the water from wells Jb45-3 and Lb24-1 (Figures 10 and 11). This indicates that denitrification is not the cause of the low nitrate concentrations. The plots of the ions in water from these two wells are in the same area in Figures 10 and 11, as are the same ions in water from wells with natural water chemistry. Water in the two wells also contains higher concentrations of sodium relative to total major cations (Figure 12) and less potassium compared to chloride (Figure 14) than most agricultural wells. These wells are close to domestic septic systems and effluent from a septic system is probably the source of ions influencing the water chemistry. Sodium concentrations in water affected by sewage should be higher than other major cations because sodium is the major cation in sewage (Table 3).

Chloride concentration is high relative to that of potassium in water from well Pe25-2, as is the ratio of the sodium concentration to the concentration of total major cations (Figure 12). This is probably indicative of effluent from a septic tank. The trends of dissolved ions in water in this well, however, follow the agricultural trends of increasing calcium plus magnesium and potassium with increasing nitrates (Figures 10 and 11). The chemistry of water in the well seems to be influenced by a mixture of both agricultural and domestic land uses.

More than three wells are needed to define the influence of septic-tank effluent on water chemistry. On the basis of water chemistry in the three wells discussed above (Jb45-3, Lb24-1, and Pe25-2), however, water influenced by domestic septic systems appears to have definitive characteristics as does water influenced by agriculture. The relative amounts of each chemical constituent resulting from these two different sources are not easily quantified because of variables such as plant uptake and reactions in the soil zone. Water chemistry from some wells, especially rural domestic, may be influenced by both types of land uses.

Other wells in locations with slightly different land-use patterns also show some variations in water chemistry when compared to the dominant trends for agricultural wells. For example, wells Nb34-4, Kb23-2, and Kb42-9 are on dairy farms. Water from well Nb34-4 has the highest ammonium plus organic nitrogen concentration (2.7 mg/L) of all the wells sampled. This concentration is an indication that the nitrogen species have not been fully oxidized and may be the reason why the concentration of nitrate is less than the trend in concentration for agricultural wells (Figure 9). Water from wells Kb23-2 and Kb42-9 has a higher potassium concentration, which seems to be high compared to that of chloride (Figure 14). The chemistry of the water in the two wells may be an indication of manure, lack of plant uptake of potassium in a feedlot, or some other variation in chemical input or land use.

The highest nitrate concentration of water sampled, 40 mg/L as nitrogen, occurred in well Qe44-3. This concentration is probably related to the well's proximity to a chickenhouse.

Another important characteristic of the chemistry of water in the unconfined aquifer is the inverse relation between nitrate and bicarbonate concentrations (Figure 13). Bicarbonate is the major anion in most natural water samples and in all anoxic water samples. The bicarbonate concentration is less than 0.16 mmol/L (9.8 mg/L) in all but one of the oxygenated water samples that have more than 0.16 mmol/L (2.3 mg/L as nitrogen) nitrate.

Bicarbonate concentration is apparently depleted in oxic water by a buffering reaction with hydrogen ions produced by nitrification. (See Reactions 7 and 8, p. 27 and Reaction 10, p. 35). However, owing to this buffering, the pH of water from the unconfined aquifer is not necessarily lowered by nitrification. There is no obvious trend of low pH with high nitrate concentrations as one might expect from nitrification in the absence of buffering (Figure 15).

Production of  $1/2$  mole  $\text{NO}_3^-$  through nitrification can result in depletion of 1 mole  $\text{HCO}_3^-$ . Thus, even small concentrations of nitrogen species undergoing nitrification can influence the relative proportions of bicarbonate to nitrate in water with low natural bicarbonate concentrations.

### Iron

Dissolved iron is a common constituent of anoxic water and its concentration generally increases with increasing bicarbonate concentration (Figure 16). Because nitrate is unstable in a

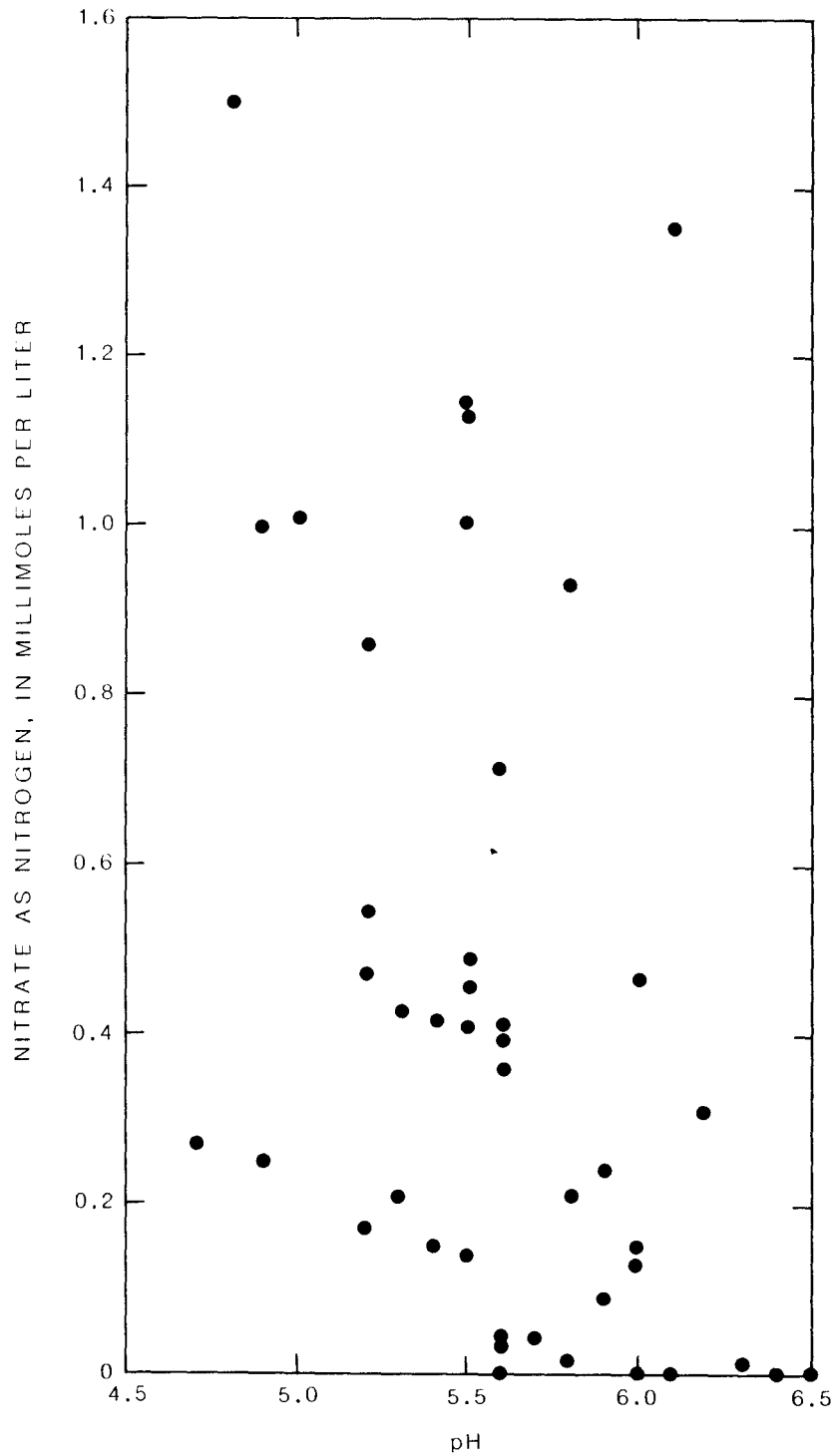


Figure 15. Relation of nitrate concentration to pH for water in the unconfined aquifer.

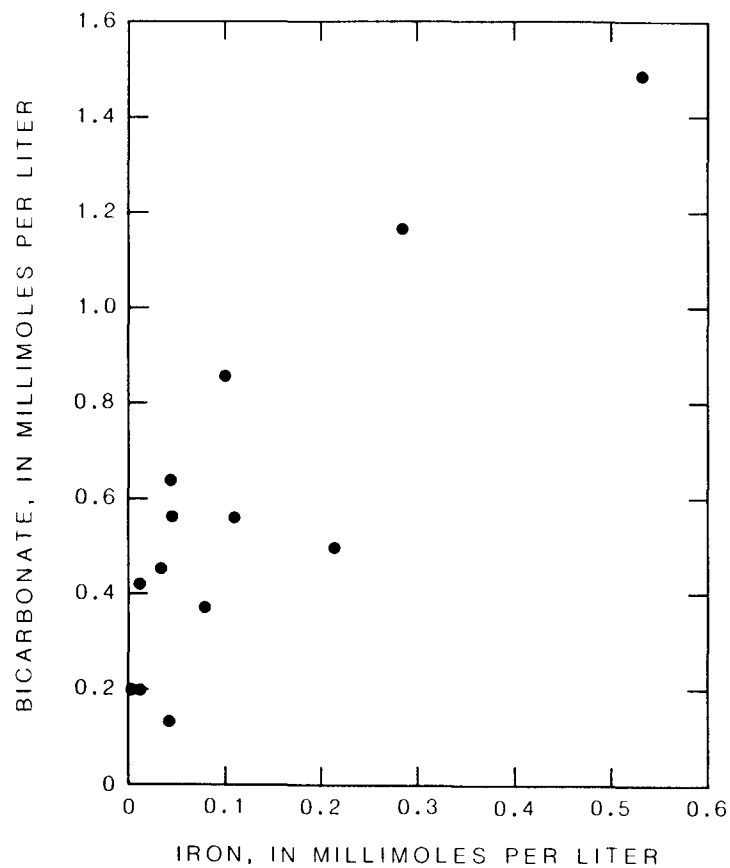


Figure 16. Relation of bicarbonate concentration to iron concentration for anoxic water in the unconfined aquifer.



reducing environment, an inverse correlation between iron and nitrate in the water samples exists (Figure 17). Water in some of the wells contains both nitrate and dissolved iron, an indication that the water is not at equilibrium.

The wells with water containing high dissolved iron (Kc41-1, 6.4 mg/L; Lc42-1, 13 and 16 mg/L; Lc42-2, 27 and 30 mg/L; and Of11-1, 12 mg/L) are located in poorly drained soils. Most of the wells where dissolved iron concentration of the water exceeded 0.3 mg/L (the secondary drinking water standard) were screened near the base of the aquifer. Several of these wells are also in the subcrop area of an aquifer in the Chesapeake Group. The dissolved oxygen in the water from these wells was probably depleted as the water moved through the flow system. Soil permeability probably does not control the oxidation potential in these wells.

High concentrations of phosphorus and sulfate are associated with high concentrations of iron. This relation is probably due

to the higher pH which is usually associated with anoxic water samples and to the higher organic content of poorly drained soils. Compounds of both phosphorus and sulfate are virtually insoluble in acidic soils high in iron and aluminum oxides (Brady, 1974). The solubility of phosphorus is greatest in the range of pH from 6.0 to 7.0 (Brady, 1974) and most of the water samples from reducing environments fall in this range. Although high sulfate concentrations are frequently associated with high iron and phosphorus concentrations, there is no other correlation of sulfate with soils or land use.

The two highest phosphorus concentrations (and iron concentrations) in the wells sampled are in water from wells Lc42-1 (1.1 mg/L) and Lc42-2 (0.85 mg/L). The pH values of water in these wells are also two of the highest (6.7 and 6.5) measured in the area. The phosphorus concentrations are more than an order of magnitude greater than those from the remainder of the wells sampled and are probably derived from naturally occurring organic and inorganic sources. Other phosphorus concentrations from water with high iron concentrations range from 0.04 to 0.08 mg/L. Phosphorus concentrations in most of the oxic water sampled were less than 0.03 mg/L. Most of the agricultural wells sampled are located in parts of the aquifer with oxidizing environments. Apparently the phosphorus component of fertilizer is not significantly mobile in the water sampled in the study.

#### Concurrence with Other Studies

Many of the trends of the data collected are supported by results of three other studies in the area: (1) a detailed study of a small area in western Kent County (Demicco, 1982), (2) a study of water quality as it relates to physical characteristics of the unconfined aquifer in southwestern Kent County (Harrington, 1981), and (3) a study of nitrate and iron occurrence in selected areas of Kent and Sussex counties (Ritter and Chirnside, 1982).

Demicco (1982) documented the inverse relation between iron and nitrate and observed that it closely paralleled soil type, land use, and geomorphology. Soils in wooded areas were generally poorly drained and concentrations of dissolved iron in the ground water were generally high. The concentration of dissolved iron in water from wells under fields was usually low, and concentration of nitrate was high or low. Demicco also found that the amount of nitrate in the water varied directly with chloride and calcium plus magnesium concentrations. Demicco related this correlation to agricultural practices. Other direct correlations noted by Demicco were between concentrations of

nitrate and sodium and of nitrate and sulfate. These correlations are not obvious in the water from the current study.

Harrington (1981) related high dissolved iron concentration to areas with reducing environments characterized by low topographic relief, shallow water tables, and poor drainage. She noted that land-surface elevations were higher, soils were well drained, and water tables were deeper in oxidizing environments than in reducing environments. Using statistical analysis, Harrington found significant correlations between (1) high nitrate and low iron concentrations; (2) high nitrate and high chloride concentrations; and (3) high iron and high pH values. An increase in both nitrate and chloride concentrations with increasing specific conductance was also observed.

Ritter and Chirnside (1982) were primarily interested in relating the occurrence of high nitrate concentrations in ground water to soil type and land use. They found the highest nitrate concentrations in areas of intensive poultry production, or corn and soybean production, on excessively drained soils (1982). Ritter and Chirnside (1982) concluded that poultry manure and fertilizer are the main source of nitrate contamination in the areas that they studied. Although Ritter and Chirnside (1982) found that water in low density residential areas had low nitrate concentrations, they concluded that leachate from septic tanks did contribute nitrate to the aquifer in certain areas. Water from wells in forested areas was also found to have low nitrate concentrations. The authors also noted that high iron concentrations and low nitrate concentrations were associated with poorly drained soils (1982).

The influence of soil characteristics and land-use patterns on the chemistry of the water in the unconfined aquifer is evident in the results of these other studies. The concurrence of their results with the current areal evaluation of water chemistry is significant because it demonstrates similarities in chemical processes throughout the aquifer.

#### Relation of Specific Conductance to Alkalinity

Comparison of laboratory analyses of major ions to alkalinity and specific conductance can be extrapolated to provide a general means of interpreting water chemistry. Bicarbonate is the major component of alkalinity and is the predominant anion in anoxic water and in oxic water under natural conditions. Bicarbonate ion concentration may be depleted in oxic water, however, by nitrification. The relation between specific conductance and alkalinity depends on which of these

variables is dominant in the aquifer.

The relation of alkalinity to specific conductance for all wells sampled is shown in Figure 18. As conductivity increases, alkalinity increases in water identified as having natural water chemistry, or a reducing environment, or both. Water from wells without laboratory analyses that follow the trend shown in Figure 18 probably have similar chemical characteristics. Water whose alkalinity values are less than 10 mg/L over a wide range of specific conductance values are probably affected by nitrification related to land use. As land-use influence increases, so does specific conductance. For specific conductance greater than 120  $\mu\text{S}/\text{cm}$ , the nitrate concentration of all but three of the wells sampled for laboratory analysis is greater than 10 mg/L as nitrogen (Figure 18B). Because of the predominance of water with nitrate concentrations exceeding 10 mg/L, nitrate concentrations of wells with similar alkalinity-specific conductance relations probably exceed the drinking water standards. Thus, measurement of field alkalinity and specific conductance can be used as a rapid, inexpensive tool to indicate whether nitrate concentration is higher than acceptable, and, whether a determination of nitrate is necessary.

Certain land-use and soil characteristics also relate to the two major trends between alkalinity and specific conductance. Most of the wells with natural water chemistry (16 of 24) or high iron concentrations, or both (8 of 10), are in wooded areas (see Figures 18A and B). The wells with water whose concentration of iron is high are usually beneath poorly drained, anoxic soils. Alkalinity concentration of water in all the agricultural wells, except one, is 10 mg/L or less (Figure 18A), an indication that those processes that deplete alkalinity in the aquifer, such as nitrification, influence water chemistry even at very low concentrations of hydrogen ion production.

Data collected in Maryland by Bachman and Wilson (1984) from 80 wells in the unconfined aquifer adjacent to the study area were plotted in Figure 19 to test the relation between specific conductance and alkalinity of water from the Delaware study area. The Maryland data were collected primarily from October 1982 to January 1983 and include specific conductance and concentrations of alkalinity, nitrate, and iron. Most data from the Delaware wells were collected from June 1982 to October 1983.

Trends in the Maryland data are similar to those in the Delaware data: increasing alkalinity with increasing specific conductance and low alkalinity over a wide range of specific conductance. The area of nitrate concentration exceeding 10 mg/L as nitrogen is not as well defined in the Maryland data as it is

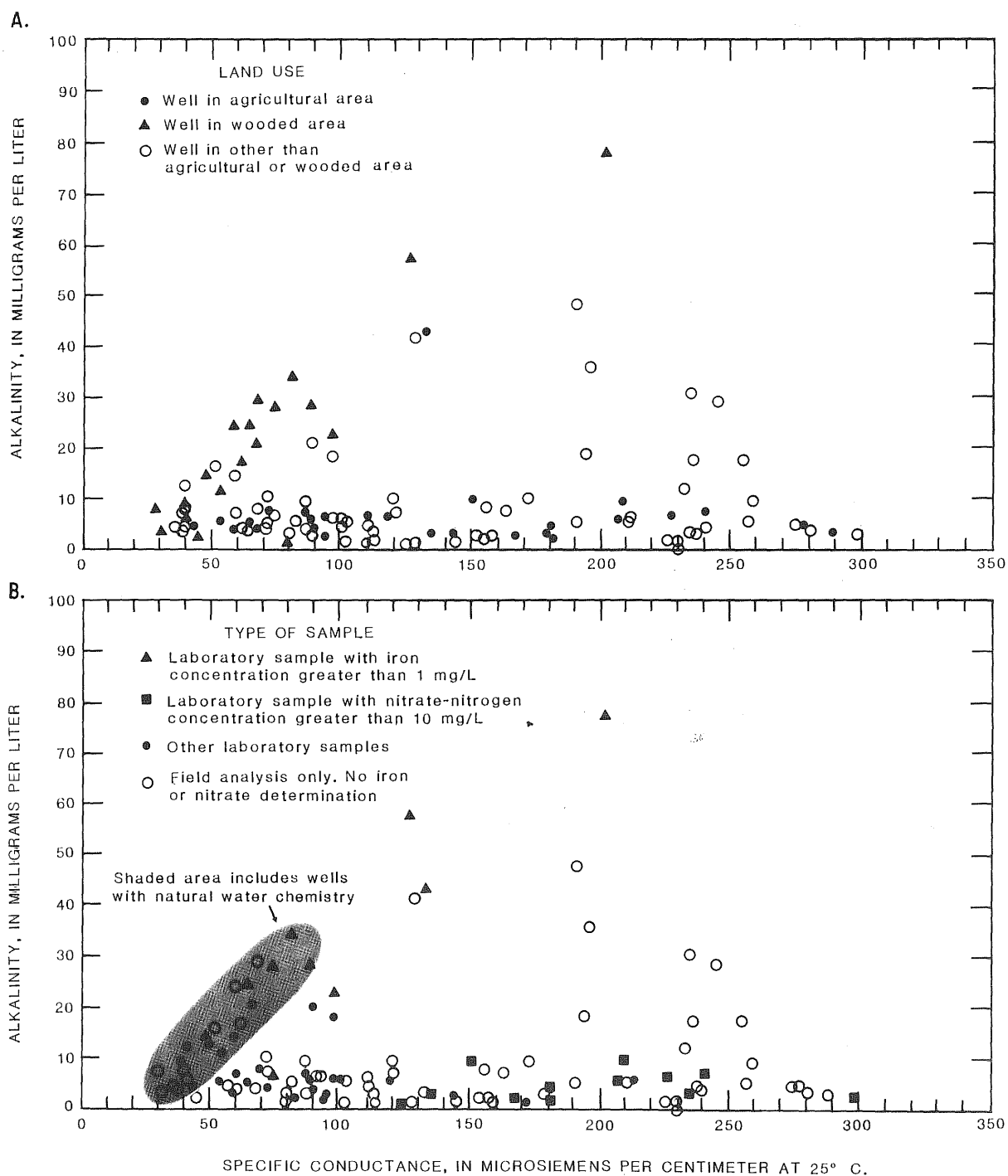


Figure 18. Relation of alkalinity concentration to specific conductance for water in the unconfined aquifer.

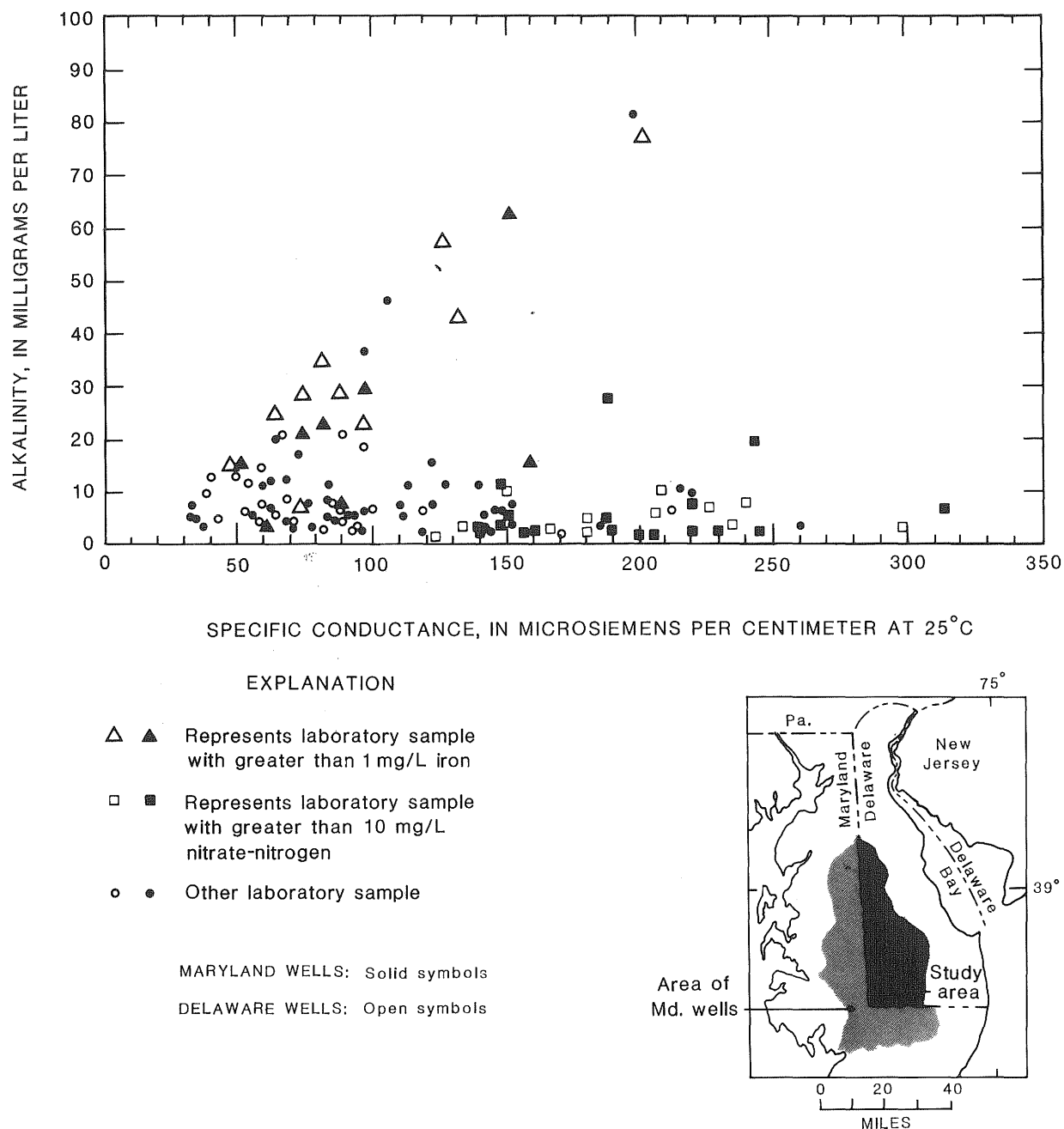


Figure 19. Relation of alkalinity concentration to specific conductance for water in the unconfined aquifer in Maryland and Delaware.

in the Delaware data. This difference may be related to a seasonal variation in nitrate concentration because the samples were collected at different times, or to different land uses associated with the sampled wells.

Of the 36 Maryland wells with specific conductances greater than 120  $\mu\text{S}/\text{cm}$ , nitrate concentrations of 18 wells are greater than 10 mg/L as nitrogen. Nitrate concentration of an additional 8 wells is greater than 8 mg/L. In the remaining wells, with nitrate concentration less than 8 mg/L, ammonium plus organic nitrogen concentrations are greater than or equal to 0.7 mg/L. Chloride and nitrate concentrations of these wells would plot below the trend shown in Figure 9. These factors are an indication that the nitrification reactions may not be complete, probably owing to temperature controls on the nitrification process, which allow other forms of nitrogen to be leached into the aquifer. Sulfate concentration of water from the 36 Maryland wells ranges from 14 to 50 mg/L. Sulfate concentration is generally well below 10 mg/L in the other Maryland wells sampled. The low concentrations of sulfate may indicate septic effluent as a source of nitrate in the Maryland wells, as opposed to the association of agricultural practices with wells that have nitrate concentrations greater than 10 mg/L in Delaware.

#### Relation of Water Chemistry To Depth At Test Well Sites

Multiple test wells were installed at three sites to study water chemistry at different depths in the same part of the aquifer and to supplement areal evaluation of aquifer chemistry. Locations of sites are shown in Figure 2. The test sites were located where pumpage of other wells would not influence the natural flow system. The land-use and hydrogeologic character of each site represents different conditions typical of large parts of the unconfined aquifer.

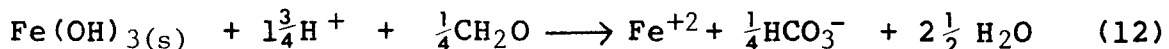
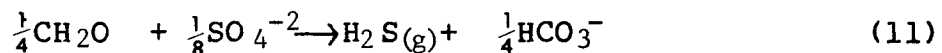
##### Site 1

Site 1 is in an area of predominantly poorly drained soils. The wells at this site are screened at depths of 20 to 25 feet (Lc42-2) and 50 to 55 feet (Lc42-1) below land surface in sediments of the Columbia Formation. The base of the Columbia Formation, which coincides with the base of the unconfined aquifer, is 67 feet below land surface. Water-level fluctuations in the wells indicate hydraulic connection (Figure 20) between them. The chemical analyses of water from wells Lc42-1 and Lc42-2 are similar (Appendix 1 Table 11). Differences in water chemistry between the wells are apparently related to land use and redox

potential in the recharge areas.

Sodium and chloride concentrations are higher in water in well Lc42-2, the shallower well, than water in well Lc42-1. The difference is probably due to a varying influence of land use. Leachate from a domestic septic system upgradient from the wells is the likely source of influence because sodium and chloride are major constituents of septic effluent. Calcium and magnesium concentrations are not elevated in water from either well, as one might expect with liming, so agricultural use of land is not as likely a source. The deeper well, Lc42-1, appears to be slightly influenced by septic effluent, but the effects of the effluent are not as concentrated deeper in the flow system. Chloride and ammonium plus organic nitrogen concentrations are slightly higher in the second measurement of the wells than in the first. This could be related to an increase in the influence of septic effluent on the water in both wells.

Other characteristics of the water from the two wells are related to the reduction of iron and sulfur species. Dissolved iron concentration of water in both wells is high, and dissolved oxygen concentration is zero. Such concentrations are indicative of reducing conditions. Hydrogen sulfide gas was also noticed in each well. Concentrations of iron and alkalinity were higher and sulfate was lower in Lc42-2, the shallower well, than in Lc42-1, the deeper well. The odor of hydrogen sulfide gas was stronger in well Lc42-2 than in Lc42-1. These changes in chemistry indicate a greater degree of reduction and a further progression of the following reactions which show oxidation of organic matter and reduction of iron and sulfate to produce hydrogen sulfide:



Homeowners in the area reported wide variations in dissolved-iron concentration of the ground water over short distances. This variation, and the variation of constituents in water from the test wells, seems to be related to changes in soil characteristics in the recharge areas that affect redox potential. Areal variation in soil characteristics was obvious from comparison of a soil boring at the well site with two other borings within 100 feet of the site. The soil at the well site, mostly silt and clay, is mottled to the land surface. A boring in a cultivated field near the wells found 3 feet of sand at the surface overlying a dense, gray, clay layer. Sand beneath the clay layer is mottled. At another boring site in the woods near the wells, 4 feet of sand overlies a layer of cemented sediments,



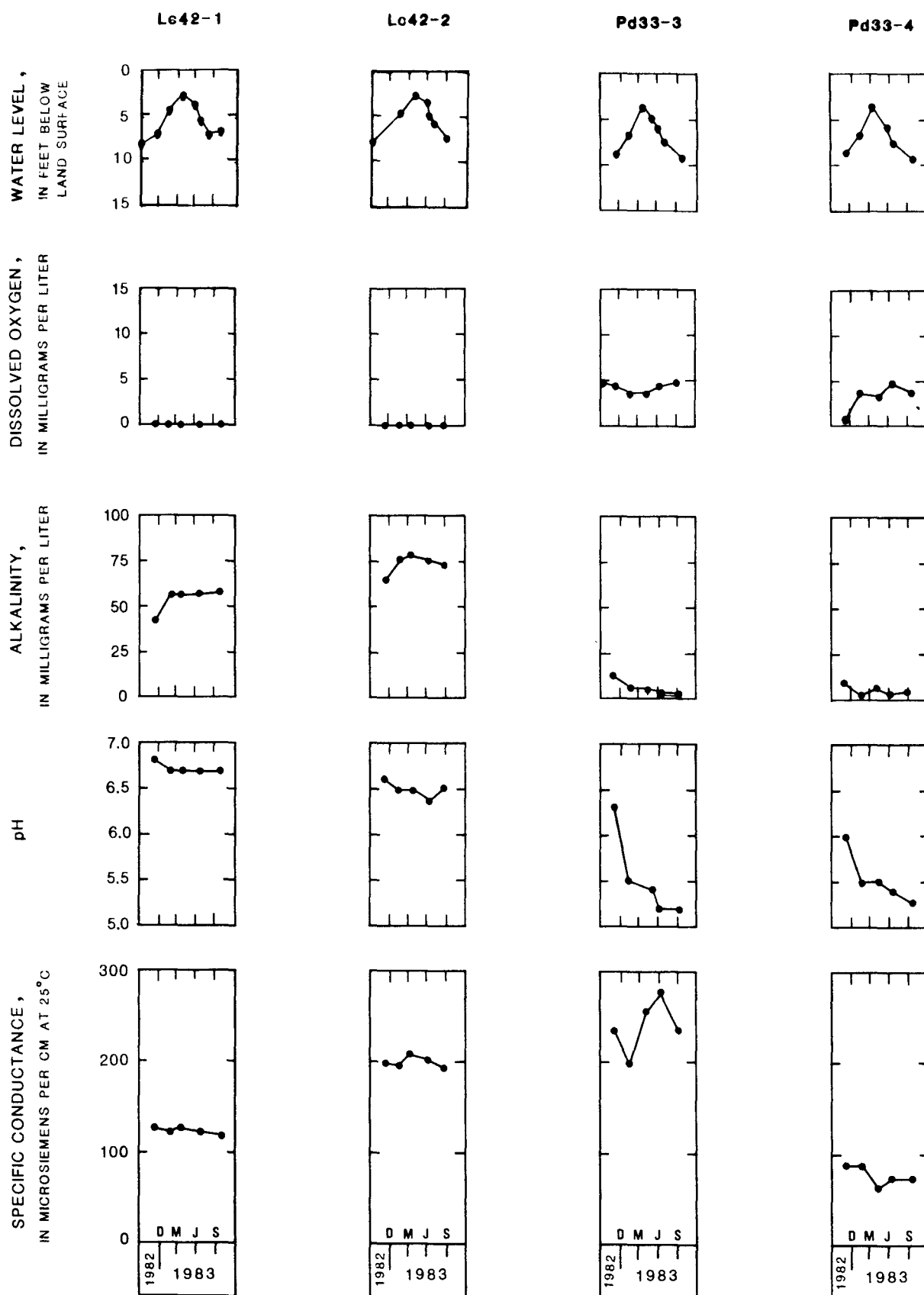
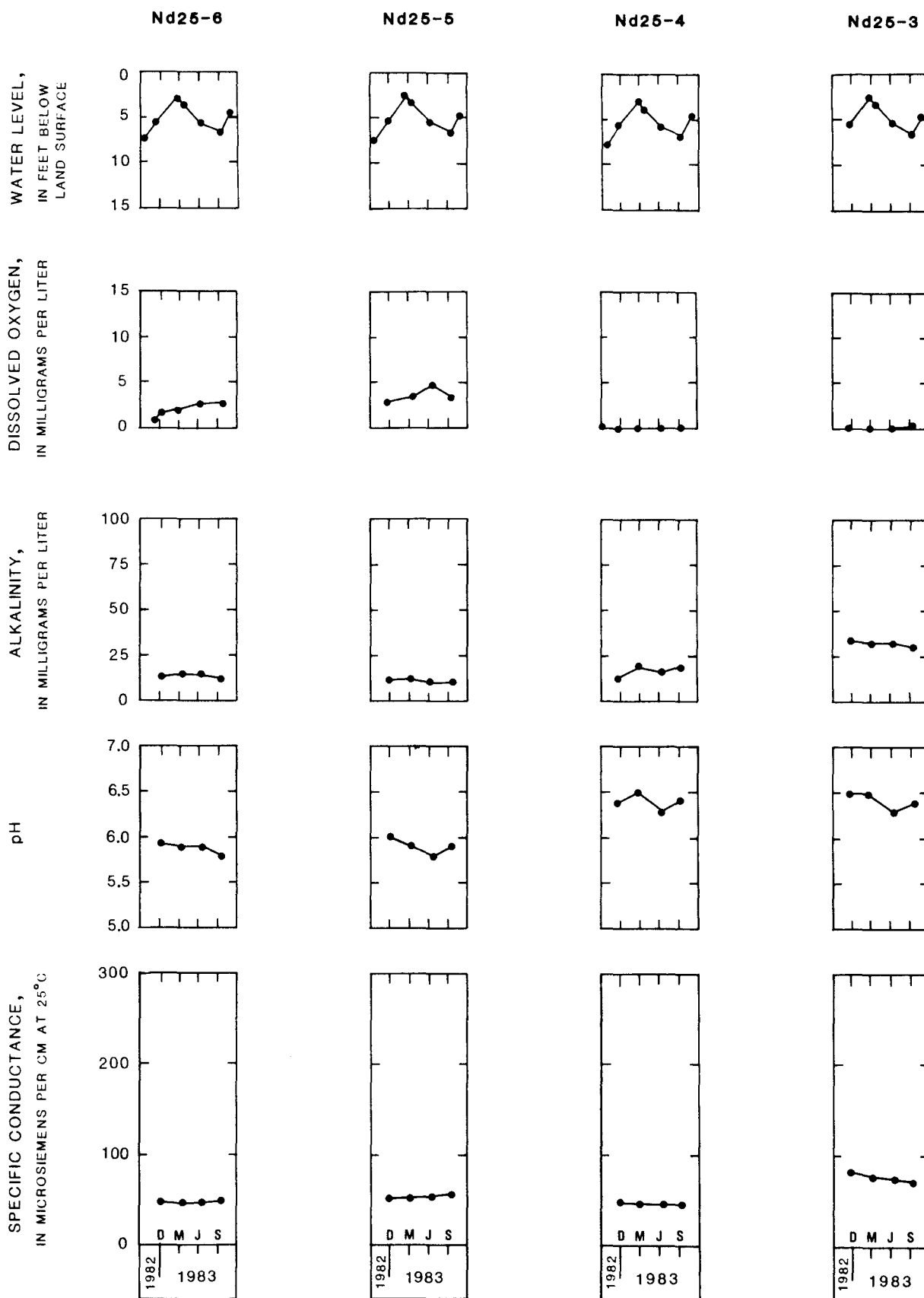


Figure 20. Water levels , dissolved oxygen, alkalinity, pH, and specific conductance for wells at test sites, October 1982 to December 1983.



probably iron oxides, that could not be penetrated. This cemented layer is probably a contact between oxidizing and reducing environments.

## Site 2

Site 2 is in a predominantly wooded area of poor to moderately well-drained soils. The wells are screened from 38 to 43 feet (Nd25-6), 49 to 54 feet (Nd25-5), 85 to 90 feet (Nd25-4), and 112 to 117 feet (Nd25-3) below land surface. The two shallowest wells are screened in sediments of the Beaverdam Formation, and the two deepest wells are screened in the Columbia Formation. The contact between the Beaverdam and Columbia formations is about 80 feet below land surface. At 117 feet below land surface, the sediments change from coarse orange sand and gravel to gray sand. This is probably the contact between the Columbia Formation and the Manokin aquifer of the Chesapeake Group. The uniform fluctuation of water levels in the four wells is indicative of a hydraulic connection among them (Figure 20).

Chemical analyses of water from the four wells are indicative of natural water chemistry for the unconfined aquifer, except for the analyses of water in well Nd25-5, which seem to indicate influence of land use. Water chemistry and redox potential of the two shallowest and the two deepest wells differ. Water in the shallowest wells is oxic. In the deepest wells, the water has been in the flow system longer and most or all of the dissolved oxygen has been consumed by reactions with oxidizable compounds in the sediments.

In the two shallowest wells the geologic features of the aquifer are the same, but differences in the chemistry of the water (Table 11) indicate that the recharge areas for the depths screened by the two wells are different. The deeper of the two wells, Nd25-5, has concentrations of nitrate, calcium, magnesium, sodium, potassium, and chloride slightly higher than those in Nd25-6. Because the silica concentration is not proportionally higher in Nd25-5, which would indicate a greater degree of silicate dissolution, the water in this part of the aquifer is probably affected by an anthropogenic source.

The water chemistry in the deeper wells, Nd25-3 and Nd25-4, also differs (Table 11). Well Nd25-4 has the lowest specific conductance and concentration of calcium, magnesium, and potassium of the four wells. Conversely, concentrations of silica and iron were the highest measured for the four wells. The concentrations of ions in Nd25-3 indicate an increase in silicate mineral weathering when compared to the concentrations of ions in

the shallower wells. Water chemistry in the part of the aquifer screened by Nd25-4 cannot be explained using available data.

There are significant differences in sediments in the screened interval of the deeper wells which may affect mineral weathering and, therefore, contribute to the differences in water chemistry. Well Nd25-3 is screened in coarse sand and gravel at the base of the Columbia Formation in contact with fine sand of the Manokin aquifer. Well Nd25-4 is screened in a coarse gravel and produced 17 gal/min when pumped, compared to 2 gal/min for the other wells at the site.

### Site 3

Site 3 is in an agricultural area of predominantly well-drained and excessively well-drained soils. The wells at the site are screened from 42 to 47 feet (Pd33-3) and 89 to 94 feet (Pd33-4) below land surface. The shallower well is screened in orange coarse sand and gravel, probably the Columbia Formation. The deeper well is screened in gray sand interbedded with silt layers, probably the Manokin aquifer. The contact between the Columbia and Manokin sediments appears to be about 52 feet below land surface and the base of the unconfined aquifer is 112 feet below land surface. Because of the similarity in fluctuation of water levels in these wells (Figure 20), the aquifers are probably hydraulically connected.

The water chemistry of the wells is influenced by land use. Nitrate as nitrogen concentrations in water from well Pd33-3, the shallower well, were 16 mg/L (2-18-83) and 20 mg/L (10-4-83), and concentrations of calcium, magnesium, sodium, potassium, and chloride were proportionally elevated (Table 11). Concentrations of ions in the water from well Pd33-4 were greater than natural concentrations, but much lower than those in water from well Pd33-3. Fertilizer applied to farmland is the most likely source of these ions.

The lower ionic concentration of water in well Pd33-4 is probably due to dilution of the constituents in the shallower well by water that is not affected by land use in the deeper part of the flow system. Surficial effects on the deeper aquifer may also be impeded or blocked by a layer of finer grained sediments directly beneath the Columbia Formation. The higher silica concentration in the water from well Pd33-4 may be due to a longer contact time between water and aquifer materials than that in well Pd33-3, but the effects of added ions mask most of the characteristics of silicate hydrolysis.

The fluctuations in water chemistry of wells Pd33-3 and Pd33-4 may be related to variations in the influence of ions leached from surface application of fertilizer and lime. Alkalinity (Figure 20) and pH in both wells were highest in the winter and decreased during the remainder of the sampling period (Figure 20). In cold weather when soil bacteria are inactive, alkalinity would not be depleted by reaction with hydrogen ions produced by nitrification. Water recharging the aquifer, therefore, would have a higher alkalinity.

An increase in the concentration of most constituents, including nitrate, is accompanied by an increase in specific conductance, as shown in Table 11. The concentrations of most dissolved ions in water from well Pd33-3 were lower in the first sample taken in February than in the sample taken after the growing season in October. Therefore, specific conductance (Figure 20) is an indication of an increase in nitrification, probably from fertilizer application at the beginning of the growing season. The specific conductance (and nitrate concentrations) of the water from Pd33-4 was highest in February and lower after the growing season (Figure 20). Influence of fertilizers probably does not reach the deeper well (Pd33-4) as quickly as it does the shallower well, and the effects of land use are delayed as well as diluted.

#### Trace Metals

Concentrations of common trace metals were determined for all the water samples sent to the laboratory. The results are summarized in Table 5. Complete analyses are included in Table 11 in Appendix I. Comparison of the reported values to the range of values for bulk precipitation in the north-central and northeastern United States (Peters and Bonelli, 1982) indicates that most of the trace metals could be accounted for by atmospheric precipitation. Several of these metals, including copper, zinc, manganese, molybdenum, and cobalt, are also added to fertilizers as micronutrients that could leach into the ground water and many are found in accessory minerals in the sediments.

Barium, manganese, zinc, and strontium are found in virtually all the water sampled and at generally higher concentrations than those of the other trace metals. The highest barium concentrations are usually associated with irrigation and farm wells which have high nitrate values. The barium is probably from barite ( $\text{BaSO}_4$ ), an impurity in the dolomite which is applied to the fields.

TABLE 5. Ranges of concentration and sample size for selected trace metals and fluoride in water from the unconfined aquifer.

[All concentrations shown in micrograms per liter]

<u>Constituent</u>	<u>Range of concentration</u>	<u>Number of observations above detection limits</u>
Aluminum	<10 - 400	34
Barium	30 - 710	58
Beryllium	<0.5 - 2	16
Cadmium	<1 - 4	15
Cobalt	<3 - 100	27
Copper	<10 - 90	15
Fluoride	<100 - 200	8
Lead	<10 - 30	14
Lithium	<4 - 21	10
Manganese	<1 - 570	57
Molybdenum	<10 - 20	8
Strontium	11 - 690	58
Vanadium	<6 - 11	5
Zinc	3 - <sup>1</sup> 320	56

<sup>1</sup> Does not include zinc concentrations influenced by galvanized well casing.

High manganese concentrations are also associated with water containing high nitrate concentrations. Water from reducing environments with a high iron concentration also usually has a high manganese concentration. Manganese concentration in most water exceeds the secondary drinking water standard of 50 micrograms per liter (U.S. Environmental Protection Agency, 1975) where either iron or nitrate exceeds the respective standards (0.3 mg/L and 10 mg/L as nitrogen).

Zinc exceeded the drinking water standard (5 mg/L) in two of the wells sampled, Kc14-2 (7 mg/L) and Mc51-1 (6.6 mg/L). The casings of both of these wells are galvanized steel, and the wells are primarily used for water-table observation. Zinc concentrations may build up in water surrounding the well owing to oxidation and dissolution of the coating of zinc on the casing. The range of zinc concentrations in the rest of the wells sampled can be accounted for by precipitation and micronutrients.

Some strontium in the water could be attributed to precipitation, but mineral sources probably account for most of it. Strontium can replace potassium and calcium in igneous rocks and calcium in carbonate rocks such as dolomite. There is a direct relation between concentrations of strontium and calcium (Figure 21) in water from irrigation wells. Thus, dolomite applied to fields to increase crop production seems to be a major source of strontium in the ground water.

#### MINERAL EQUILIBRIA RELATIONS

Consideration of the equilibrium relations between ground water and aquifer materials in the unconfined aquifer is limited by the influence of land use on water chemistry. Redox potential and dissolution of silicate minerals, however, can be examined by use of calculated stability relations, and chemical mass balance can be calculated for wells with natural and virtually natural water chemistry. WATEQF, a computer program that calculates chemical equilibrium (Plummer and others, 1976), was used to calculate the speciation of elements and stabilities of various minerals with respect to water samples representing different aquifer conditions. The accuracy of the element speciation and mineral stabilities calculated by WATEQF depends on the accuracy of chemical and thermodynamic input data, and on the assumption that the natural system was in equilibrium when the water sample was collected.

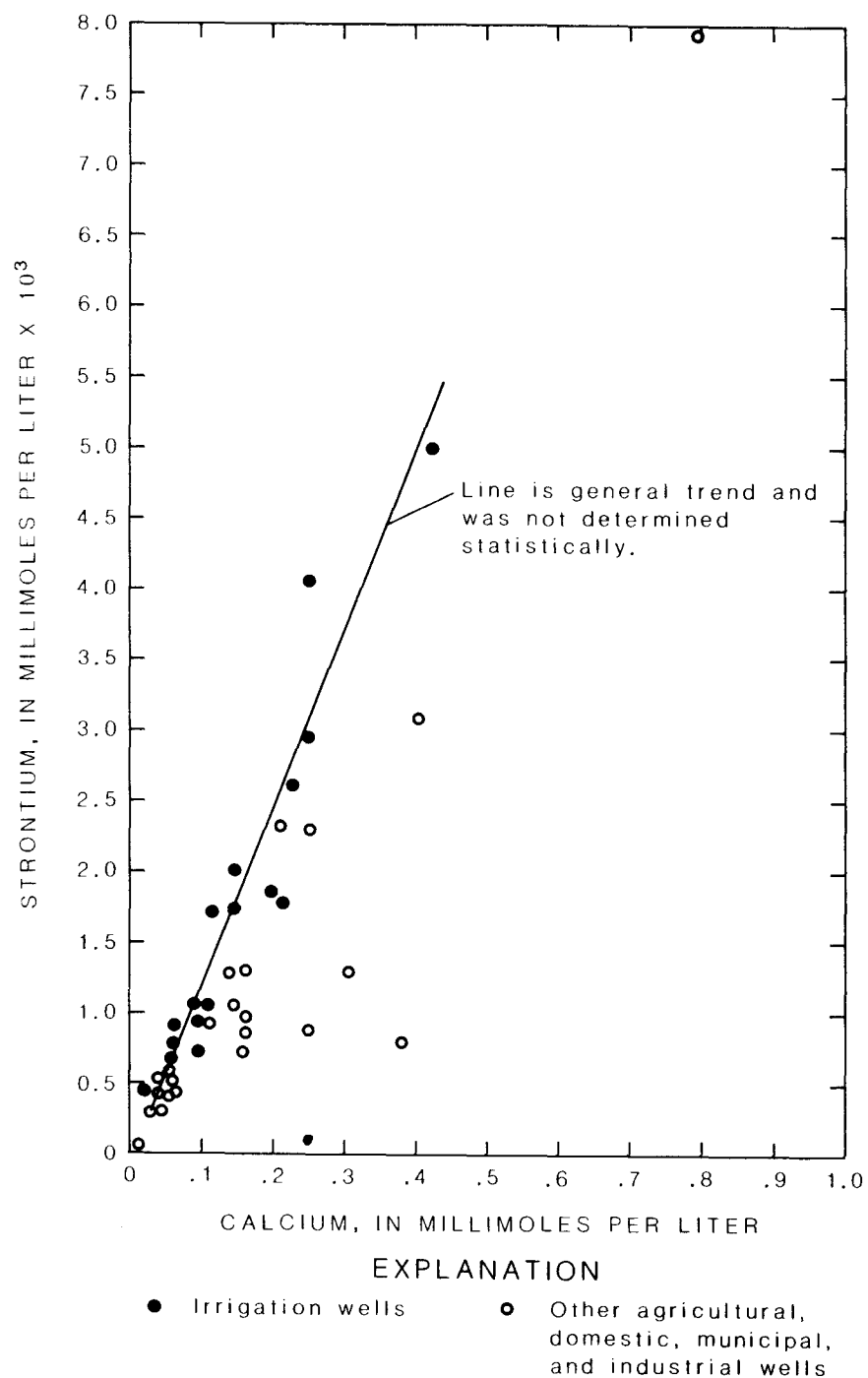


Figure 21. Relation of strontium concentration to calcium concentration for water in the unconfined aquifer.



### Silicate Dissolution

The main alteration product of incongruent dissolution of feldspars in most ground-water systems is kaolinite. Plots of water analyses on silicate mineral stability diagrams (Figure 22) show that kaolinite is a stable phase in ground water in Delaware. The ratios of  $\text{Na}^+/\text{H}^+$  and  $\text{Ca}^{2+}/\text{H}^+$  are shown to increase as the concentration of dissolved silica increases, and the ratio of  $\text{K}^+/\text{H}^+$  also seems to increase slightly. These trends are an indication of increasing feldspar dissolution (Freeze and Cherry, 1979). When cation and silica concentrations increase sufficiently, montmorillonite may become a stable phase in this system.

The aluminum concentrations used as input to WATEQF were adjusted so that the stability calculations were at equilibrium with kaolinite. The concentrations used were generally lower than those measured in the water because aluminum is strongly influenced by complexing. Many of its complexed forms are converted to micro-crystalline particles (Hem, 1970) that cannot be removed by filtering.

The adjusted aluminum concentrations were then used to calculate the saturation indices of micas, gibbsite, illite, and calcium, sodium, and potassium feldspars. These minerals were shown to be undersaturated in the unconfined aquifer. Any of these minerals present in the aquifer are unstable and will dissolve leaving kaolinite as a residual solid. Montmorillonite was slightly supersaturated in many of the samples and, where present, would be stable. Quartz and chalcedony were slightly supersaturated in most of the samples, whereas the lower-grade silica gel and silica glass were undersaturated. On the basis of these indices, incongruent dissolution of silicate minerals is assumed to be the major source of dissolved silica in the water even though the more resistant quartz is the most common form of silica in the sediments.

### Mass-Balance Calculations

Mass-balance calculations were attempted for several of the chemical analyses that represent natural or virtually natural water in the aquifer. These calculations were made for the purpose of comparing the products of the chemical reactions that are considered to be active in the aquifer to those in the observed water chemistry. The reactions considered are shown in Table 6 and are a simplified representation of the natural system. They are not the only set of reactions that could produce the observed water chemistry, but, rather, are the

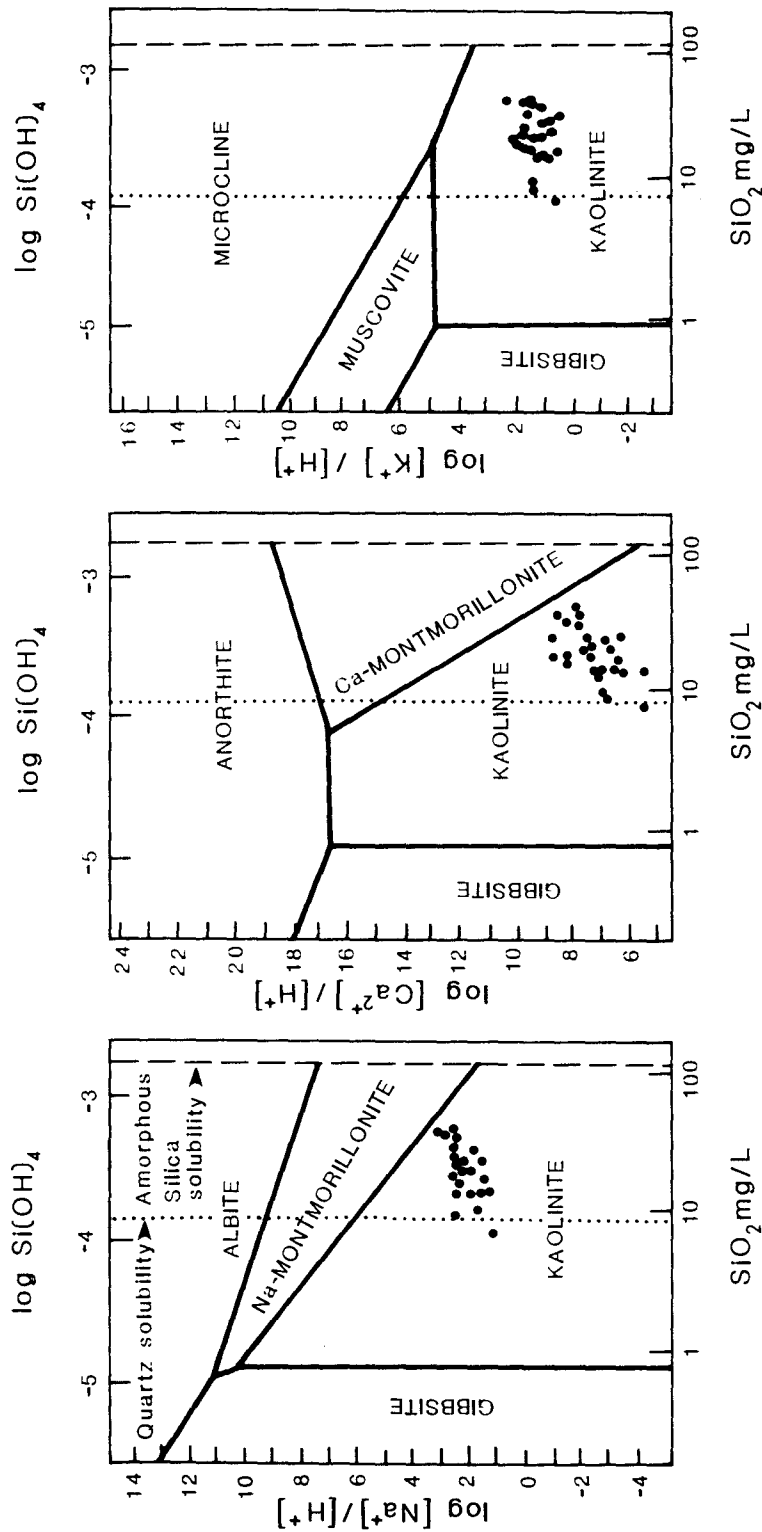
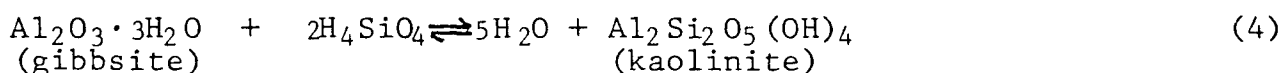
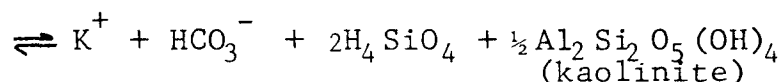
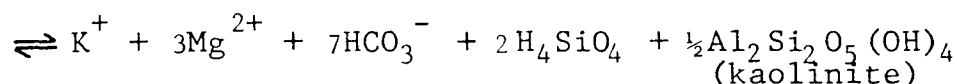
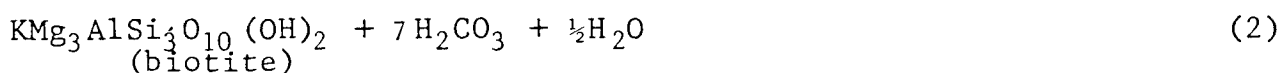
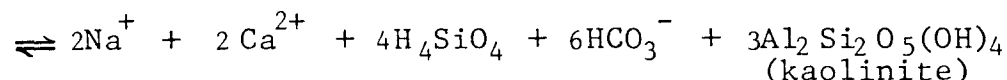
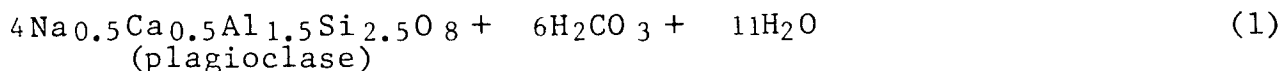
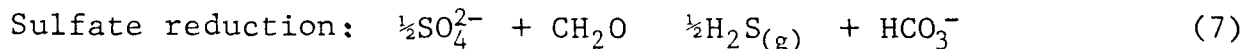
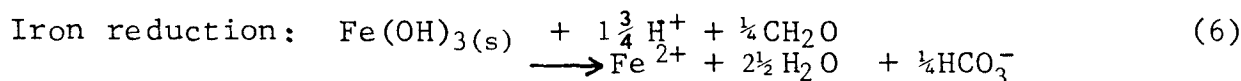
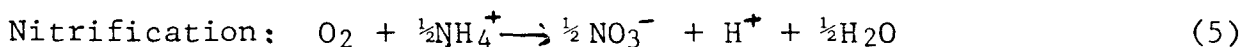
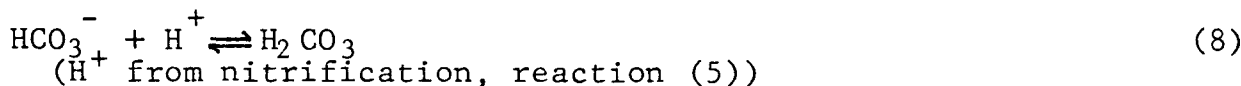


Figure 22. Analyses of water from the unconfined aquifer plotted on silicate-mineral stability diagrams. ( Modified after Freeze and Cherry, 1979, p. 272.)

TABLE 6. Reactions used in calculating chemical mass balances of water from the unconfined aquifer.

Incongruent dissolution reactions:Redox reactions:Bicarbonate depletion:

probable reactions based on knowledge of aquifer mineralogy and composition of recharge water.

Accurate laboratory and field analyses are difficult to obtain for water of low concentrations of dissolved solutes, such as those in the water of the unconfined aquifer. The charge balance for these samples usually consists of more anions than cations. Alkalinity, pH, and specific conductance of water from anoxic zones of the aquifer may change significantly between measurement in the field and analysis in the laboratory probably owing to precipitation of ferric hydroxide in the sample bottles. These changes and the charge balance need to be considered and to be compensated for in the mass-balance calculations.

Ions in atmospheric precipitation can be a significant factor in mass-balance calculations of ground water that have low concentrations of dissolved solutes. Several assumptions are made about the effects of precipitation on water chemistry. All the chloride in the water and a proportional amount of sodium is assumed to be from precipitation. These concentrations are subtracted from the initial concentrations as are sulfate and nitrate concentrations at or below the average concentrations in precipitation (Table 2). These subtractions account for some of the excess negative charges in the initial solution. Any remaining sulfate or nitrate concentrations are used to evaluate excess or depleted bicarbonate concentrations (Reactions 7 and 8, Table 6).

Mass-balance calculations are shown in Table 7. The basic reactions of silicate dissolution are the same for all the calculations. All the calculations result in excess dissolved silica that is not accounted for through the production of kaolinite by the incongruent dissolution of silicates. This excess silica can be accounted for, however, by gibbsite in the sediments. Although gibbsite is not a stable phase, its formation as a product of silicate weathering results in greater amounts of dissolved silica in ground water than does the formation of kaolinite. The relation between these minerals is shown in Table 6, Reaction 4.

The total calcium concentration, and the concentration of sodium remaining after subtraction of sodium attributed to precipitation, are assumed to result from dissolution of plagioclase (Table 6, Reaction 1). The ratio between sodium and calcium is not known from aquifer mineralogy and is assumed to be influenced by cation exchange. Biotite was chosen as a mica phase for these calculations to account for the magnesium concentrations of the water.

TABLE 7. Mass-balance calculations for removal of constituents derived by natural processes in water of the unconfined aquifer.

Well: Lb24-1 (oxic water)									
Chemical process	Constituent balance, millimoles per liter								
	Ca <sup>+2</sup>	Mg <sup>+2</sup>	Na <sup>+</sup>	K <sup>+</sup>	HCO <sub>3</sub> <sup>-</sup>	Cl <sup>-</sup>	NO <sub>3</sub> <sup>-</sup>	SO <sub>4</sub> <sup>-2</sup>	SiO <sub>2</sub>
Concentration of ions in initial ground water	0.04	0.03	0.38	0.02	0.16	0.27	0.15	0.01	0.47
Remove ions from precipitation (table 2) and oxidation of organic matter (sulfate)	0.04	0.03	0.11	0.02	0.16	0	0.09	0	0.47
Balance calcium and sodium by cation exchange	0.075	0.03	0.075	0.02	0.16	0	0.09	0	0.47
Remove dissolved plagioclase (table 6, eq. 1)	0	0.03	0	0.02	-0.07	0	0.09	0	0.32
Remove dissolved biotite (table 6, eq. 2)	0	0	0	0.01	-0.14	0	0.09	0	0.30
Remove dissolved orthoclase (table 6, eq. 3)	0	0	0	0	-0.15	0	0.09	0	0.28
Remove dissolved silica by formation of gibbsite <sup>1</sup> (table 6, eq. 4)	0	0	0	0	-0.15	0	0.09	0	0
Remove excess nitrate and account for deficient bicarbonate with nitrification (table 6, eqs. 5 and 8)	0	0	0	0	0.03	0	0.09	0	0

Well: Lc42-1 (anoxic water)									
Chemical process	Constituent balance, millimoles per liter								
	Ca <sup>+2</sup>	Mg <sup>+2</sup>	Na <sup>+</sup>	K <sup>+</sup>	HCO <sub>3</sub> <sup>-</sup>	Cl <sup>-</sup>	NO <sub>3</sub> <sup>-</sup>	SO <sub>4</sub> <sup>-2</sup>	SiO <sub>2</sub>
Concentration of ions in initial ground water	0.16	0.06	0.31	0.03	1.14	0.17	0	0.30	0.58
Remove ions from precipitation (table 2) and oxidation of organic matter (sulfate)	0.16	0.06	0.15	0.03	1.14	0	0	0	0.58
Balance calcium and sodium by cation exchange	0.155	0.06	0.155	0.03	1.14	0	0	0	0.58
Remove dissolved plagioclase (table 6, eq. 1)	0	0.06	0	0.03	0.68	0	0	0	0.28
Remove dissolved biotite (table 6, eq. 2)	0	0	0	0.01	0.55	0	0	0	0.24
Remove dissolved orthoclase (table 6, eq. 3)	0	0	0	0	0.54	0	0	0	0.23
Remove dissolved silica by formation of gibbsite <sup>1</sup> (table 6, eq. 4)	0	0	0	0	0.54	0	0	0	0
Remove bicarbonate produced through iron and sulfate reduction (table 6, eqs. 6 and 7)	0	0	0	0	0	0	0	0	0

Well: Md55-2 (oxic water)									
Chemical process	Constituent balance, millimoles per liter								
	Ca <sup>+2</sup>	Mg <sup>+2</sup>	Na <sup>+</sup>	K <sup>+</sup>	HCO <sub>3</sub> <sup>-</sup>	Cl <sup>-</sup>	NO <sub>3</sub> <sup>-</sup>	SO <sub>4</sub> <sup>-2</sup>	SiO <sub>2</sub>
Concentration of ions in initial ground water	0.05	0.01	0.24	0.01	0.26	0.12	0.02	0.01	0.50
Remove ions from precipitation (table 2) and oxidation of organic matter (sulfate)	0.05	0.01	0.12	0.01	0.26	0	0.01	0	0.50
Balance calcium and sodium by cation exchange	0.085	0.01	0.085	0.01	0.26	0	0.01	0	0.50
Remove dissolved plagioclase (table 6, eq. 1)	0	0.01	0	0.01	0.01	0	0.01	0	0.50
Remove dissolved biotite (table 6, eq. 2)	0	0	0	0.01	-0.01	0	0.01	0	0.32
Remove dissolved orthoclase (table 6, eq. 3)	0	0	0	0	-0.02	0	0.01	0	0.31
Remove dissolved silica by formation of gibbsite <sup>1</sup> (table 6, eq. 4)	0	0	0	0	-0.02	0	0.01	0	0
Remove excess nitrate and account for deficient bicarbonate with nitrification (table 6, eqs. 5 and 8)	0	0	0	0	0	0	0	0	0

TABLE 7. Mass-balance calculations for removal of constituents derived by natural processes in water of the unconfined aquifer--Continued.

Well: Nd25-3 (anoxic water)									
Chemical process	Constituent balance, millimoles per liter								
	Ca <sup>+2</sup>	Mg <sup>+2</sup>	Na <sup>+</sup>	K <sup>+</sup>	HCO <sub>3</sub> <sup>-</sup>	Cl <sup>-</sup>	NO <sub>3</sub> <sup>-</sup>	SO <sub>4</sub> <sup>-2</sup>	SiO <sub>2</sub>
Concentration of ions in initial ground water	0.07	0.03	0.44	0.03	0.64	0.13	0	0.03	0.57
Remove ions from precipitation (table 2) and oxidation of organic matter (sulfate)	0.07	0.03	0.31	0.03	0.64	0	0	0	0.57
Balance calcium and sodium by cation exchange	0.19	0.03	0.19	0.03	0.64	0	0	0	0.57
Remove dissolved plagioclase (table 6, eq. 1)	0	0.03	0	0.03	0.08	0	0	0	0.20
Remove dissolved biotite (table 6, eq. 2)	0	0	0	0.02	0.02	0	0	0	0.18
Remove dissolved orthoclase (table 6, eq. 3)	0	0	0	0	0	0	0	0	0.14
Remove dissolved silica by formation of gibbsite <sup>1</sup> (table 6, eq. 4)	0	0	0	0	0	0	0	0	0

Well: Nd25-4 (anoxic water)									
Chemical process	Constituent balance, millimoles per liter								
	Ca <sup>+2</sup>	Mg <sup>+2</sup>	Na <sup>+</sup>	K <sup>+</sup>	HCO <sub>3</sub> <sup>-</sup>	Cl <sup>-</sup>	NO <sub>3</sub> <sup>-</sup>	SO <sub>4</sub> <sup>-2</sup>	SiO <sub>2</sub>
Concentration of ions in initial ground water	0.02	0.01	0.31	0.01	0.36	0.17	0	0.04	0.58
Remove ions from precipitation (table 2) and oxidation of organic matter (sulfate)	0.02	0.01	0.14	0.01	0.36	0	0	0	0.58
Balance calcium and sodium by cation exchange	0.08	0.01	0.08	0.01	0.36	0	0	0	0.58
Remove dissolved plagioclase (table 6, eq. 1)	0	0.01	0	0.01	0.12	0	0	0	0.42
Remove dissolved biotite (table 6, eq. 2)	0	0	0	0.01	0.11	0	0	0	0.42
Remove dissolved orthoclase (table 6, eq. 3)	0	0	0	0	0.10	0	0	0	0.40
Remove dissolved silica by formation of gibbsite <sup>1</sup> (table 6, eq. 4)	0	0	0	0	0.10	0	0	0	0
Remove bicarbonate produced through iron and sulfate reduction (table 6, eqs. 6 and 7).	0	0	0	0	0	0	0	0	0

Well: Nd25-5 (oxic water)									
Chemical process	Constituent balance, millimoles per liter								
	Ca <sup>+2</sup>	Mg <sup>+2</sup>	Na <sup>+</sup>	K <sup>+</sup>	HCO <sub>3</sub> <sup>-</sup>	Cl <sup>-</sup>	NO <sub>3</sub> <sup>-</sup>	SO <sub>4</sub> <sup>-2</sup>	SiO <sub>2</sub>
Concentration of ions in initial ground water	0.06	0.02	0.31	0.02	0.21	0.13	0.16	0.01	0.38
Remove ions from precipitation (table 2) and oxidation of organic matter (sulfate)	0.06	0.02	0.18	0.02	0.21	0	0.10	0	0.38
Balance calcium and sodium by cation exchange	0.12	0.02	0.12	0.02	0.21	0	0.10	0	0.38
Remove dissolved plagioclase (table 6, eq. 1)	0	0.02	0	0.02	-0.16	0	0.10	0	0.14
Remove dissolved biotite (table 6, eq. 2)	0	0	0	0.02	-0.19	0	0.10	0	0.10
Remove dissolved orthoclase (table 6, eq. 3)	0	0	0	0	-0.21	0	0.10	0	0.08
Remove dissolved silica by formation of gibbsite <sup>1</sup> (table 6, eq. 4)	0	0	0	0	-0.21	0	0.10	0	0
Remove excess nitrate and account for deficient bicarbonate with nitrification (table 6, eqs. 5 and 8)	0	0	0	0	-0.01	0	0	0	0

TABLE 7. Mass-balance calculations for removal of  
constituents derived by natural processes in  
water of the unconfined aquifer--Continued.

Well: Nd25-6 (oxic water)									
Chemical process	Constituent balance, millimoles per liter								
	Ca <sup>+2</sup>	Mg <sup>+2</sup>	Na <sup>+</sup>	K <sup>+</sup>	HCO <sub>3</sub> <sup>-</sup>	Cl <sup>-</sup>	NO <sub>3</sub> <sup>-</sup>	SO <sub>4</sub> <sup>-2</sup>	SiO <sub>2</sub>
Concentration of ions in initial ground water	0.06	0.02	0.29	0.02	0.28	0.12	0.11	0.01	0.38
Remove ions from precipitation (table 2) and oxidation of organic matter (sulfate)	0.06	0.02	0.17	0.02	0.28	0	0.05	0	0.38
Balance calcium and sodium by cation exchange	0.115	0.02	0.115	0.02	0.28	0	0.05	0	0.38
Remove dissolved plagioclase (table 6, eq. 1)	0	0.02	0	0.02	-0.05	0	0.05	0	0.16
Remove dissolved biotite (table 6, eq. 2)	0	0	0	0.01	-0.08	0	0.05	0	0.15
Remove dissolved orthoclase (table 6, eq. 3)	0	0	0	0	-0.10	0	0.05	0	0.12
Remove dissolved silica by formation of gibbsite <sup>1</sup> (table 6, eq. 4)	0	0	0	0	-0.10	0	0.05	0	0
Remove excess nitrate and account for deficient bicarbonate with nitrification (table 6, eqs. 5 and 8)	0	0	0	0	0	0	0	0	0
Well: Ne54-3 (anoxic water)									
Chemical process	Constituent balance, millimoles per liter								
	Ca <sup>+2</sup>	Mg <sup>+2</sup>	Na <sup>+</sup>	K <sup>+</sup>	HCO <sub>3</sub> <sup>-</sup>	Cl <sup>-</sup>	NO <sub>3</sub> <sup>-</sup>	SO <sub>4</sub> <sup>-2</sup>	SiO <sub>2</sub>
Concentration of ions in initial ground water	0.03	0.02	0.19	0.03	0.20	0.14	0	0.02	0.23
Remove ions from precipitation (table 2) and oxidation of organic matter (sulfate)	0.03	0.02	0.05	0.03	0.20	0	0	0	0.23
Balance calcium and sodium by cation exchange	0.04	0.02	0.04	0.03	0.20	0	0	0	0.23
Remove dissolved plagioclase (table 6, eq. 1)	0	0.02	0	0.03	0.08	0	0	0	0.15
Remove dissolved biotite (table 6, eq. 2)	0	0	0	0.02	0.05	0	0	0	0.14
Remove dissolved orthoclase (table 6, eq. 3)	0	0	0	0	0.02	0	0	0	0.09
Remove dissolved silica by formation of gibbsite <sup>1</sup> (table 6, eq. 4)	0	0	0	0	0.02	0	0	0	0
Remove bicarbonate produced through iron and sulfate reduction (table 6, eqs. 6 and 7).	0	0	0	0	0	0	0	0	0
Well: Pe54-4 (anoxic water)									
Chemical process	Constituent balance, millimoles per liter								
	Ca <sup>+2</sup>	Mg <sup>+2</sup>	Na <sup>+</sup>	K <sup>+</sup>	HCO <sub>3</sub> <sup>-</sup>	Cl <sup>-</sup>	NO <sub>3</sub> <sup>-</sup>	SO <sub>4</sub> <sup>-2</sup>	SiO <sub>2</sub>
Concentration of ions in initial ground water	0.01	0.05	0.39	0.02	0.56	0.22	0	0.04	0.52
Remove ions from precipitation (table 2) and oxidation of organic matter (sulfate)	0.01	0.05	0.17	0.02	0.56	0	0	0	0.52
Balance calcium and sodium by cation exchange	0.09	0.05	0.09	0.02	0.56	0	0	0	0.52
Remove dissolved plagioclase (table 6, eq. 1)	0	0.05	0	0.02	0.16	0	0	0	0.25
Remove dissolved biotite (table 6, eq. 2)	0	0	0	0.01	0.05	0	0	0	0.22
Remove dissolved orthoclase (table 6, eq. 3)	0	0	0	0	0.04	0	0	0	0.20
Remove dissolved silica by formation of gibbsite <sup>1</sup> (table 6, eq. 4)	0	0	0	0	0.04	0	0	0	0.20
Remove bicarbonate produced through iron and sulfate reduction (table 6, eqs. 6 and 7).	0	0	0	0	0	0	0	0	0

<sup>1</sup>/ Assumption that excess silica is due to formation of gibbsite instead of kaolinite during weathering of silicates.

Oxidation or reduction of nitrogen, manganese, iron, or sulfate affects bicarbonate concentration of ground water. The amount of bicarbonate resulting from silicate dissolution is generally less than the theoretical amount in the mass-balance calculations of oxic water. The amount of bicarbonate needed can be accounted for by assuming that nitrate concentration in excess of the average amount from precipitation results from the oxidation of organic and ammonium nitrogen. The amount of bicarbonate that is depleted as a result of combining with the excess hydrogen ions produced through nitrification (Table 6, Reactions 5 and 8) is nearly the amount needed to balance the reactions of silicate dissolution.

Mass-balance calculations that include silicate dissolution for anoxic water yield an excess of bicarbonate. This excess is attributed to iron and sulfate reduction (Table 6, Reactions 6 and 7). The exact amount of bicarbonate produced by each process cannot be quantified because hydrogen sulfide gas was not measured when the water samples were collected. The presence of hydrogen sulfide gas during sampling and observation of precipitation of iron minerals in water samples exposed to the atmosphere are physical evidence that these processes are active in a reducing ground-water environment.

Sulfate in ground water in excess of the amount from precipitation is attributed to the oxidation of organic sulfur in the soil zone or to organic material in the sediments. There are no significant amounts of sulfide minerals in aquifer sediments that could account for high sulfate concentrations.

On the basis of the mass-balance calculations (Table 7), the natural water chemistry of the unconfined aquifer could be the result of dissolution of the primary silicate minerals in the aquifer influenced by redox processes. Acceptable mass-balance results can be attained even though there is some potential for error in the assumptions pertaining to the chemical system and the techniques used in analyzing dilute water samples.

### Iron Speciation

Total dissolved-iron concentration of the water is the sum of many dissolved-iron species and complexes. The oxidation potential in the aquifer and the iron species available for reaction control the occurrence and speciation of dissolved iron. WATEQF was used to calculate the speciation of dissolved iron and to examine the saturation states of iron minerals that could contribute dissolved iron to the water.



Goethite  $[\text{FeO}(\text{OH})]$  and amorphous ferric hydroxide  $[\text{Fe}(\text{OH})_3]$  are the most common iron minerals in the surficial sediments. Hem and Cropper (1959) found that the behavior of  $\text{Fe}(\text{OH})_3(\text{s})$  was the chief control on iron solubility in natural water. WATEQF calculations for water in the unconfined aquifer agree with their results: Goethite is saturated (stable) in oxidizing and reducing environments, whereas  $\text{Fe}(\text{OH})_3(\text{s})$  is saturated or very near equilibrium in oxic water and is always undersaturated (unstable) in reducing water. Thus,  $\text{Fe}(\text{OH})_3(\text{s})$  enters into dissolution and precipitation reactions more readily than goethite.

Certain species of dissolved iron are dominant under several conditions even though iron speciation is very complex. The iron speciation calculated by WATEQF and examples of speciation in oxidizing and reducing environments are shown in Table 8. Although  $\text{Fe}(\text{OH})_2^+$  is the dominant ion in oxic water,  $\text{Fe}^{+2}$  is dominant in anoxic water. This relation holds for all the water samples in which dissolved iron was detected.

The  $\text{Fe}(\text{OH})_2^+$  ion was also determined by WATEQF calculations to be the dominant ferric iron species in solution in oxic water of the Patuxent Formation in Maryland (Chapelle, 1985). This was verified by use of a stability diagram showing total iron as a function of pH. A similar stability diagram was constructed with data from the unconfined aquifer for showing equilibrium relations between amorphous  $\text{Fe}(\text{OH})_3$  and ferric ions (Figure 23). Concentrations of total iron as a function of pH for water analyses in oxic water fit the boundary of  $\text{Fe}(\text{OH})_2^+(\text{aq})$  and  $\text{Fe}(\text{OH})_3(\text{s})$ . This agrees with the iron speciation calculated by WATEQF, which shows that  $\text{Fe}(\text{OH})_2^+$  is the predominant dissolved-iron species in oxic water of the unconfined aquifer.

Dissolved-iron species in oxic water are in the  $\text{Fe}^{+3}$  oxidation state. Dissolved iron in reducing water is in the  $\text{Fe}^{+2}$  oxidation state. Variations in pH and in oxidation potential, also called "redox potential," result in changes in the stability of various iron species. These variations, as they relate to water in the unconfined aquifer, can be illustrated by use of iron stability diagrams.

Stability diagrams were constructed by using thermodynamic data and chemical equilibria relations between the major solid and dissolved iron species. Detailed description of the construction of these diagrams is given in Garrels and Christ (1965). Generally, the diagrams shown in Figure 24 illustrate the stability fields of solid and dissolved forms of iron in an aqueous system in terms of Eh and pH. Sulfate and bicarbonate ion concentrations are also considered because these are common constituents of water in the unconfined aquifer that may be

TABLE 8. Iron speciation used by WATEQF for calculating mineral equilibria in water from the unconfined aquifer.

Species	Rc22-5, oxic water (millimoles/liter)	Of11-1, anoxic water (millimoles/liter)
Fe <sup>+2</sup>	7.66 x 10 <sup>-12</sup>	2.14 x 10 <sup>-1</sup>
Fe <sup>+3</sup>	1.44 x 10 <sup>-8</sup>	8.34 x 10 <sup>-17</sup>
FeOH <sup>+2</sup>	3.30 x 10 <sup>-6</sup>	4.25 x 10 <sup>-13</sup>
FeOH <sup>+</sup>	7.80 x 10 <sup>-17</sup>	5.24 x 10 <sup>-5</sup>
Fe(OH) <sub>3</sub> <sup>-</sup>	5.72 x 10 <sup>-29</sup>	1.61 x 10 <sup>-14</sup>
Fe(OH) <sub>2</sub> <sup>+</sup>	2.47 x 10 <sup>-4</sup>	2.84 x 10 <sup>-10</sup>
Fe(OH) <sub>3</sub>	2.21 x 10 <sup>-7</sup>	4.06 x 10 <sup>-12</sup>
Fe(OH) <sub>4</sub> <sup>-</sup>	1.83 x 10 <sup>-10</sup>	5.30 x 10 <sup>-14</sup>
Fe(OH) <sub>2</sub>	2.05 x 10 <sup>-23</sup>	3.48 x 10 <sup>-10</sup>
FeHPO <sub>4</sub> <sup>+</sup>	6.98 x 10 <sup>-12</sup>	1.68 x 10 <sup>-18</sup>
FeHPO <sub>4</sub>	3.67 x 10 <sup>-17</sup>	5.56 x 10 <sup>-5</sup>
FeH <sub>2</sub> PO <sub>4</sub> <sup>+</sup>	1.04 x 10 <sup>-15</sup>	9.54 x 10 <sup>-5</sup>
FeH <sub>2</sub> PO <sub>4</sub> <sup>+2</sup>	1.83 x 10 <sup>-9</sup>	2.63 x 10 <sup>-17</sup>
FeSO <sub>4</sub> <sup>+</sup>	6.80 x 10 <sup>-10</sup>	1.12 x 10 <sup>-17</sup>
FeCl <sup>+2</sup>	8.54 x 10 <sup>-11</sup>	3.06 x 10 <sup>-19</sup>
FeCl <sub>2</sub> <sup>+</sup>	4.49 x 10 <sup>-13</sup>	4.48 x 10 <sup>-22</sup>
FeCl <sub>3</sub>	1.82 x 10 <sup>-17</sup>	8.58 x 10 <sup>-27</sup>
FeSO <sub>4</sub>	9.38 x 10 <sup>-15</sup>	7.12 x 10 <sup>-7</sup>

= dominant species.

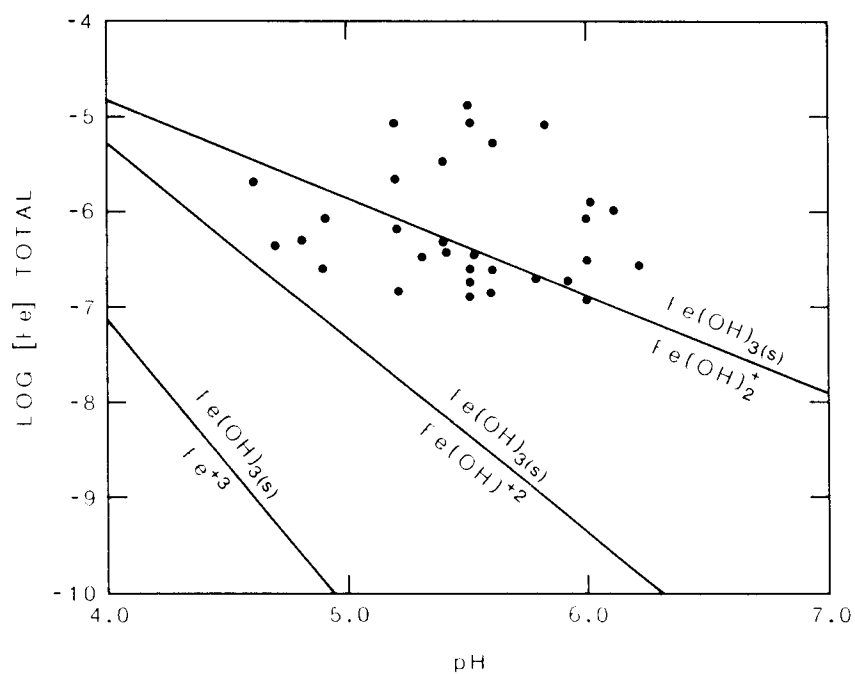


Figure 23. Relation of the log activity of iron to pH for water in the unconfined aquifer with equilibrium boundaries between  $\text{Fe}(\text{OH})_{3(s)}$  and  $\text{Fe}^{+3}$ ,  $\text{Fe}(\text{OH})^{+2}$ , and  $\text{Fe}(\text{OH})_2^{+}$ . ( Modified after Chapelle, 1985. )

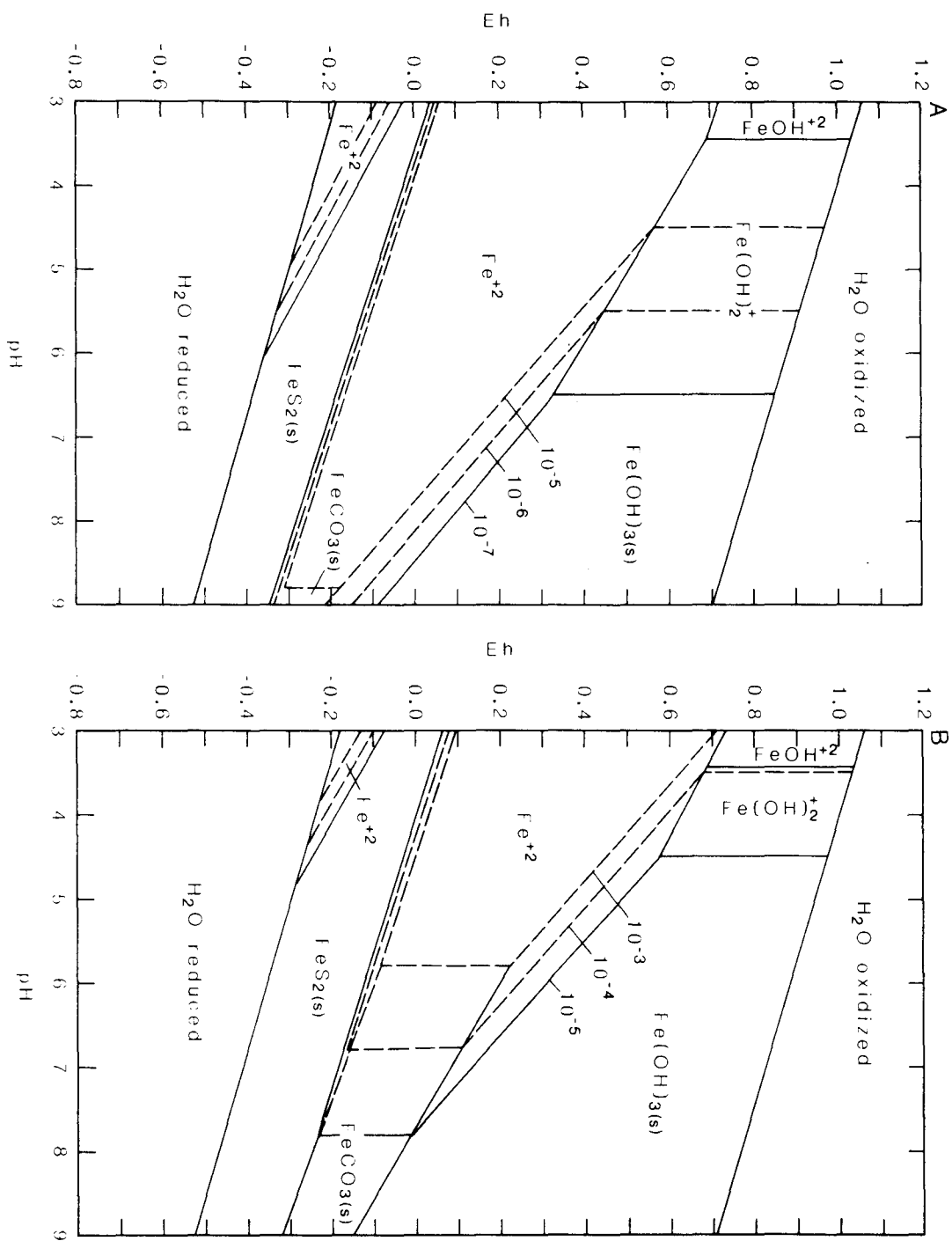


Figure 24. Relation of solubility of iron to Eh and pH at 25°C and 1 atmosphere.

Diagram A-- Total dissolved sulfate,  $10^{-4}$  moles (9.6 mg/L); bicarbonate,  $10^{-4}$  moles (6.1 mg/L);

total dissolved iron species,  $10^{-5}$  to  $10^{-7}$  moles (0.56 to 5.6  $\times 10^{-3}$  mg/L).

Diagram B-- Total dissolved sulfate,  $10^{-4}$  moles (9.6 mg/L); bicarbonate,  $10^{-3}$  moles (61 mg/L);

total dissolved iron species,  $10^{-3}$  to  $10^{-5}$  moles (56 to 0.56 mg/L).

involved in precipitation and dissolution reactions with iron. The concentrations of these components must be specified on the diagrams.

Reduction of ferric ( $\text{Fe}^{+3}$ ) to ferrous ( $\text{Fe}^{+2}$ ) iron species involves addition of an electron to the iron ion (Table 9, Reaction 1). Because these reactions are reversible, oxidation of the reduced form ( $\text{Fe}^{+2}$ ) involves loss of an electron. Eh is a measure of the potential of species in an aqueous solution to gain or lose electrons. Equilibria that involve redox reactions are therefore dependent on Eh. Equilibria not involving redox reactions involve the transfer of hydrogen ions ( $\text{H}^{+}$ ) and are, as a result, dependent on pH only.

Two Eh-pH stability diagrams were constructed by using concentrations of dissolved iron, sulfate, and bicarbonate that are typical of those for oxic and anoxic water from the unconfined aquifer (Figure 24). The stability fields represent the dominant iron species in water that can be plotted in those parts of the diagram. Other species may also be present, but at much lower concentrations than those shown by stability fields. The same thermodynamic data used by WATEQF (Plummer and others, 1976) were used to construct these diagrams.

The  $\text{Fe}(\text{OH})_2^{+}$  ion is the predominant dissolved iron species in oxic water ( $10^{-7}$  mmol/L or  $5.58 \times 10^{-6}$  mg/L) of iron. As dissolved-iron concentration increases, the  $\text{Fe}(\text{OH})_2^{+}$  field decreases and the stability of amorphous  $\text{Fe}(\text{OH})_3$  increases. Reduced  $\text{Fe}^{+2}$  is the stable-iron species over a much larger range of Eh and pH than any of the oxidized forms of iron. Thus, high concentrations of dissolved iron in the unconfined aquifer can occur only in anoxic water. This relation is also significant because it explains the mechanism of iron precipitation in the aquifer and around well screens. If the Eh of a reducing water with a high dissolved-iron concentration is increased, less dissolved iron is stable in solution and  $\text{Fe}(\text{OH})_3$  will precipitate. Eh may change as the result of atmospheric oxygen being introduced during pumping, or through mixing of oxidizing and reducing water in the flow system. Changes in pH can influence iron stabilities in the same manner as changes in Eh. Eh and pH are generally interdependent because most redox reactions involve transfer of hydrogen ion (Table 9).

Pyrite ( $\text{FeS}_2$ ) and siderite ( $\text{FeCO}_3$ ) may be stable in the unconfined aquifer under anoxic conditions according to WATEQF calculations. Pyritization has been documented in soils associated with salt marshes in Delaware (Lord and Church, 1983). Thermodynamically, pyrite probably occurs in other anoxic soils as well, although this has not been documented in Delaware.

TABLE 9. Equilibria used to construct iron-stability diagrams of water in the unconfined aquifer.

(1)	$\text{Fe}^{+2} + 3\text{H}_2\text{O} = \text{Fe}(\text{OH})_3(\text{s}) + 3\text{H}^+ + \text{e}^-$	$(\text{Eh} = 1.06 - .177\text{pH} - .0592\log[\text{Fe}^{+2}])$
(2)	$\text{Fe}^{+2} + \text{H}_2\text{O} = \text{FeOH}^{+2} + \text{H}^+ + \text{e}^-$	$(\text{Eh} = .901 - .0592\text{pH})$
(3)	$\text{Fe}^{+2} + 2\text{H}_2\text{O} = \text{Fe}(\text{OH})_2^+ + 2\text{H}^+ + \text{e}^-$	$(\text{Eh} = 1.107 - .118\text{pH})$
(4)	$\text{FeOH}^{2+} + \text{H}_2\text{O} = \text{Fe}(\text{OH})_2^+ + \text{H}^+$	$(\text{pH} = 3.48)$
(5)	$\text{Fe}(\text{OH})_2^+ + \text{H}_2\text{O} = \text{Fe}(\text{OH})_3(\text{s}) + \text{H}^+$	$(\text{pH} = -\log[\text{Fe}(\text{OH})_2^+] - 0.78)$
(6)	$\text{FeOH}^{2+} + 2\text{H}_2\text{O} = \text{Fe}(\text{OH})_3(\text{s}) + \text{H}^+$	$(2\text{pH} = 2.697 - \log[\text{FeOH}^{+2}])$
(7)	$\text{FeCO}_3(\text{s}) + \text{H}^+ = \text{Fe}^{+2} + \text{HCO}_3^-$	$(\text{pH} = -\log[\text{Fe}^{+2}] - \log[\text{HCO}_3^-] - .22)$
(8)	$\text{FeCO}_3(\text{s}) + 3\text{H}_2\text{O} = \text{Fe}(\text{OH})_3(\text{s}) + \text{HCO}_3^- + 2\text{H}^+ + \text{e}^-$	$(\text{Eh} = 1.073 - .118\text{pH} + .0592\log[\text{HCO}_3^-])$
(9)	$\text{Fe}^{+2} + 2\text{H}_2\text{S}(\text{g}) = \text{FeS}_2(\text{s}) + 4\text{H}^+ + 2\text{e}^-$	$(\text{Eh} = .136 - .118\text{pH} - .0295\log[\text{Fe}^{+2}])$
(10)	$\text{FeS}_2(\text{s}) + 8\text{H}_2\text{O} = \text{Fe}^{+2} + 2\text{SO}_4^{2-} + 16\text{H}^+ + 14\text{e}^-$	$(\text{Eh} = .324 + .0042\log[\text{Fe}^{+2}] + .0084\log[\text{SO}_4^{2-}] - .067\text{pH})$
(11)	$\text{FeS}_2(\text{s}) + 8\text{H}_2\text{O} + \text{HCO}_3^- = \text{FeCO}_3(\text{s}) + 17\text{H}^+ + 2\text{SO}_4^{2-} + 14\text{e}^-$	$(\text{Eh} = .325 - .0042\log[\text{HCO}_3^-] + .0084\log[\text{SO}_4^{2-}] - .072\text{pH})$

Pyrite is a stable field in the diagrams (Figure 24) even in association with low sulfate concentrations. The relative insignificance of  $\text{SO}_4^{2-}$  in calculation of the pyrite stability field is shown by Reactions 10 and 11 in Table 9.

Stability of siderite is dependent on the concentrations of iron and bicarbonate species in the water (Reaction 7, Table 9). This dependence is shown in Figures 24A and 24B. For an iron activity of  $10^{-5}$  mmol/L, the siderite ( $\text{FeCO}_3$ ) field is much larger with a bicarbonate concentration of  $10^{-4}$  mmol/L  $\text{HCO}_3^-$  (Figure 24B) than with one of  $10^{-4}$  mmol/L (Figure 24A). The size of the stability field of siderite increases as dissolved iron activity increases (Figure 24B). Because of this expansion of the stability field, siderite could be precipitated in parts of the unconfined aquifer. A WATEQF analysis of one well, Lc42-2, indicated that siderite would precipitate. The dissolved iron ( $10^{-3.32}$  mmol/L) and bicarbonate ( $10^{-2.8}$  mmol/L) concentration and the pH of the water in well Lc42-2 were the highest of the samples collected during the study.

Although stability diagrams are useful for illustrating iron equilibria in ground water, they must be used with an understanding of their limitations. One major limitation is the accuracy of the free energy data that are available. Free energy cited for one species differs from one reference to the next. Small changes in the free energy used may produce large changes in the resulting stability field. Other assumptions are that the water is in equilibrium and at standard temperature and pressure. The conditions in the unconfined aquifer are close to standard conditions, but, especially where sulfate reduction is an active process, the water may not be in equilibrium. The stabilities of the solids for the concentrations used are shown in the diagrams. Another limitation is the assumption that only carbonate and sulfur species are reacting with iron in the water. Although these are the major species to consider, iron may also react with other solutes such as silica and chloride.

#### SUMMARY AND CONCLUSIONS

The purpose of this study was to define the water chemistry and the hydrologic and geochemical processes that control the chemical quality of water in the unconfined aquifer of west-central and southwestern Delaware. This was done by collecting data on water chemistry from wells throughout the study area and comparing these data to precipitation chemistry and mineral reactions that may take place in the hydrologic system.

Sources of dissolved constituents in the water are precipi-

tation, mineral dissolution and alteration, and chemicals applied to the land surface through anthropogenic activities.

Redox and cation exchange reactions also influence water chemistry. Redox processes are particularly important because they control the occurrence of iron and nitrate, the two major water-quality concerns in the area. The consumption of dissolved oxygen and production of carbon dioxide through oxidation of organic matter also contributes to the production of carbonic acid ( $\text{H}_2\text{CO}_3$ ), the main weathering agent of silicate minerals.

The main source of ions in water under natural and virtually natural conditions is weathering of silicate minerals such as feldspars. Sodium and bicarbonate are the major ions in natural water from the unconfined aquifer. Specific conductance of oxic water is generally less than  $60 \mu\text{S}/\text{cm}$ . Dissolved iron can be a major ion in anoxic water and the specific conductance of anoxic water is usually higher than that of oxic water. Calcium, potassium, and magnesium are also in the water, but in concentrations below those attributable to mineral dissolution and precipitation. These low concentrations are probably the result of cation exchange reactions, which favor adsorption of divalent over monovalent cations, and fixation of potassium in the lattice of certain clays. The natural source of chloride, nitrate, and sulfate in the water is usually atmospheric precipitation. Another source of sulfate is the oxidation of organic matter.

Few of the water samples from the study area represent natural conditions in the aquifer. Concentrations of chloride and nitrate of most samples are higher than the average concentrations of chloride and nitrate from precipitation and seem to be affected by anthropogenic activities to some degree. The activity with the most widespread effect on water chemistry is the application of inorganic fertilizer, manure, and crushed dolomite for agricultural crop production. Effluent from domestic septic tanks also influences water quality, but on a localized basis.

Several trends in the concentrations of major ions in the water can be related to land uses. The trends in water chemistry that are related to agricultural land use are most obvious because many of the wells sampled are irrigation wells or are adjacent to cultivated fields. Concentrations of nitrate varied directly with concentrations of chloride, potassium, and calcium plus magnesium in most of the analyses. These constituents are related to agricultural applications of potassium chloride, crushed dolomite, and nitrogen fertilizer or manure. In some wells, the chemistry of water is influenced by leachate from domestic septic systems or concentrated manure rather than by



leachate of fertilizer. A comparison of the ratio of sodium to major cations and nitrate showed that sodium concentration of water in wells influenced by leachate from domestic septic systems was greater than that of water in wells influenced by fertilizer. Sodium is the major cation in domestic sewage and the sewage does not contain an excess of cations such as potassium, calcium, and magnesium, which are common to leachate from agricultural practices.

Another characteristic of the water in the unconfined aquifer is the apparent depletion of bicarbonate by the nitrification process. Bicarbonate that occurs naturally in the aquifer, as well as that derived from dissolution of dolomite, buffers ground water by reacting with hydrogen ions produced by nitrification and other oxidation reactions. Bicarbonate concentrations were highest in anoxic water having high concentrations of dissolved iron, and evidence of reduced sulfur species. Bicarbonate concentrations of the water are directly related to dissolved iron concentrations, which are inversely related to nitrate concentrations of the water.

The chemistry of the water from most of the wells sampled is related to the land use in the vicinity of the well. In shallow wells in particular, chemical constituents that are leached into the ground water are moved vertically in the flow system toward the screen of a pumping well. High concentrations of nitrates in deep irrigation wells with long screened intervals is evidence that pumping can influence the movement of nitrates and other chemicals in the aquifer. Concentrations of nitrate and other ions in water from these wells are among the highest in the area. In wells with shorter screened intervals, the effects of land use decrease with depth in the aquifer under non-pumping conditions.

Field determinations of specific conductance and alkalinity can be used to predict general characteristics of water chemistry. Specific conductance and alkalinity are related to major ion chemistry and follow two major trends: (1) increasing specific conductance and increasing alkalinity are associated with natural water chemistry, reducing conditions, or both; and (2) water with alkalinity below 10 mg/L and specific conductance above 50  $\mu\text{S}/\text{cm}$  is generally oxic and influenced by land use. Nitrate concentration greater than 10 mg/L as nitrate is associated with a specific conductance greater than 120  $\mu\text{S}/\text{cm}$ . These trends can be used to identify water that is under natural or virtually natural conditions and to identify water with potential iron or nitrate problems without having to obtain complete chemical analyses.

Kaolinite is the stable weathering product of silicate in

the aquifer minerals according to mineral equilibria studies of water under natural conditions. Reactions between ground water and aquifer materials are capable of producing the observed water chemistry according to mass-balance calculations. However, there is an excess of dissolved silica, possibly owing to the formation of gibbsite rather than kaolinite under some aquifer conditions.

Certain species of iron dominate under several conditions in the aquifer. These conditions are controlled by redox potential of soil. Dissolved iron in oxic water is usually in the form  $\text{Fe}(\text{OH})_2^+$  and in concentrations of less than 0.1 mg/L. Most of the iron in oxic parts of the aquifer is amorphous  $\text{Fe}(\text{OH})_3$ . In anoxic parts of the aquifer, the ferrous ion is dominant in concentrations of as much as 30 mg/L. Iron stability is dependent on the redox potential of the water and the pH. Changes in either of these factors can result in solution or precipitation of iron minerals and can affect the amount of dissolved iron in the water. Precipitation of iron hydroxide,  $\text{Fe}(\text{OH})_3$ , in the aquifer or in wells is caused by mixing of iron-rich anoxic water with oxygenated water.

In areas where nitrogen species are applied at or near the land surface and the aquifer is an oxidizing environment, nitrate concentrations frequently exceed the drinking water standard of 10 mg/L as nitrogen. Concentrations of dissolved iron in anoxic water almost always exceed 0.3 mg/L (a secondary drinking water standard) because of dissolution of natural iron coatings on many of the sand grains in the sediments. As the reducing environment intensifies, hydrogen sulfide gas is produced.

The major processes that control water chemistry are determining factors in properly locating a well that will produce water of acceptable quality. Understanding natural water chemistry is also important in the prediction of anthropogenic influences on the ground-water system.

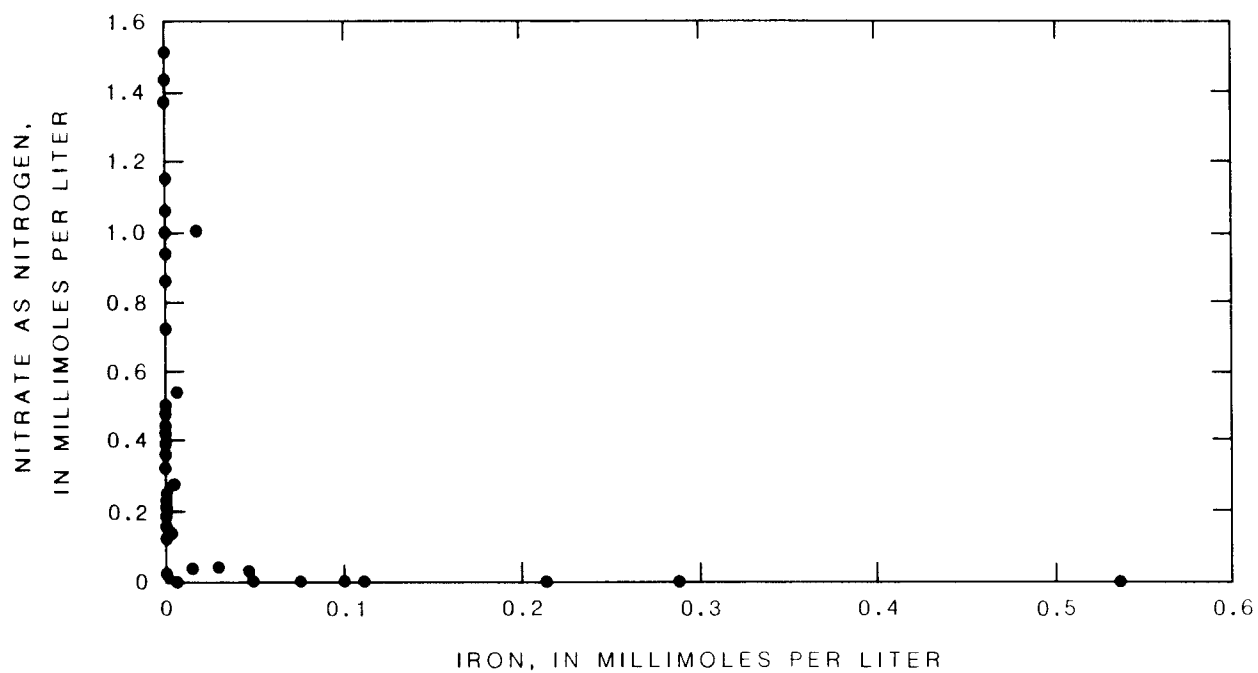
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**Figure 17.** Relation of nitrate concentration to iron concentration for water in the unconfined aquifer.

## APPENDIX I



TABLE 10. Field data from wells in the unconfined aquifer.

Soil drainage: P, poorly drained; M, moderately well-drained; E, excessively well-drained.  
 Use, well: D, domestic; A, agricultural; M, municipal; P, public; O, observation; I, industrial.  
 Use, land: O, open field, non-agricultural; R, residential; F, farm yard; W, woods; I, irrigated agriculture.

Screened interval: in feet below land surface.  
 Temp: Temperature in degrees Celsius.  
 Sp Cond: Specific conductance in micro-siemens per centimeter, at 25°C.  
 Alk: Alkalinity in milligrams per liter.  
 D.O.: Dissolved oxygen in milligrams per liter.  
 Lab?: N, no lab sample collected; Y, lab sample collected.

Well No.	Sample date	Soil drain-age	Use Well	Land	Screened interval	Temp	pH	Sp Cond	Alk	D.O.	Lab?
Jb13-7	6-16-82	P	D	O	? - 22	12.8	6.2	190	47.60	3.40	N
Jb25-1	6-23-82	P	D	W	25 - 30	16.8	4.8	102	5.74	2.00	N
Jb31-1	6-9-83	W	P	O	22 - 27	15.0	5.6	89	20.80	2.24	Y
Jb33-6	6-23-82	W	A	F	? - 30 <sup>1</sup>	14.0	6.0	236	17.20	5.65	N
Jb45-2	6-29-82	M	A	F	13 - 18	13.6	4.7	170	1.64	7.52	Y
Jb45-3	6-28-82	M	D	O	21 - 26	14.4	5.6	74	6.56	7.43	Y
Jb51-2	7-12-83	P	D	W	? - 50	17.5	6.3	59	24.60	0.00	N
Jb54-2	6-23-82	W	A	F	? - 30	12.6	5.3	210	5.74	1.30	N
Jc42-7	7-12-83	P	D	O	? - 30	18.0	5.0	101	4.92	1.00	N
Kb14-2	4-28-83	W	D	O	? - 35	13.2	6.0	196	35.40	3.68	N
Kb15-2	7-12-82	M	D	O	? - 22	15.0	4.7	128	1.64	7.17	N
Kb15-3	7-12-82	M	A	I	? - 17	14.3	5.1	274	4.92	10.10	N
Kb23-2	9-1-83	W	A	F	25 - 30	18.6	4.8	290	2.90	2.46	Y
Kb41-6	10-6-82	W	D	O	? - 50	15.2	4.9	112	3.28	3.97	N
Kb42-9	5-27-83	W	A	F	20 - 25	13.6	5.5	240	7.30	8.65	N
Kb43-2	6-24-82	M	D	O	? - 30 <sup>1</sup>	13.3	4.9	88	3.28	4.04	N
Kb45-2	6-17-82	M	D	W	? - 22	13.6	5.0	91	6.60	5.00	N
Kb51-1	10-6-82	P	D	W	? - 30 <sup>1</sup>	15.7	4.7	80	1.64	2.87	N
Kc14-2	8-11-83	P	O	W	24 - 29	14.5	6.0	67	20.90	1.35	Y
Kc14-4	6-17-82	M	D	W	? - 30	14.1	5.6	62	10.70	2.80	N
Kc35-1	5-25-83	M	D	W	? - 36	14.5	5.6	194	18.40	2.35	N
Kc41-1	6-8-83	P	D	W	27 - 32	15.0	6.0	88	28.30	0.30	Y
Kc53-1	11-2-82	P	D	W	28 - 30	15.4	6.3	238	4.92	7.31	N
Lb24-1	8-10-83	M	D	O	13 - 18	19.0	5.4	68	8.40	2.50	Y
Lb42-3	10-21-83	W	D	W	24 - 28	14.0	5.6	29	8.00	8.02	N
Lb44-2	10-4-82	M	D	O	? - 58	14.4	5.4	60	4.10	6.19	N
Lb53-1	9-29-82	P	D	O	? - 20	15.7	5.2	240	4.10	10.40	N
Lc11-1	7-12-83	W	D	O	? - 28	18.0	5.0	133	3.28	6.78	N
Lc22-1	10-7-82	P	D	W	? - 36	15.0	4.7	158	1.64	2.00	N
Lc23-3	10-7-82	M	D	O	? - 28	15.3	4.6	127	1.64	5.88	N
Lc42-1	12-15-82	P	O	O	50 - 55	11.5	6.8	128	42.64	0.00	N
	2-28-83	P	O	O	50 - 55	13.6	6.7	126	57.40	0.00	Y
	4-12-83	P	O	O	50 - 55	14.0	6.7	126	57.00	0.00	N
	7-8-83	P	O	O	50 - 55	16.5	6.7	123	57.50	0.00	N
	9-27-83	P	O	O	50 - 55	16.5	6.7	119	58.10	0.00	Y
Lc42-2	12-15-82	P	O	O	20 - 25	11.7	6.6	200	65.60	0.00	N
	2-28-83	P	O	O	20 - 25	14.0	6.5	202	77.10	0.00	Y
	4-12-83	P	O	O	20 - 25	-	6.5	209	78.70	0.00	N
	7-8-83	P	O	O	20 - 25	-	6.4	202	75.80	0.00	N
	9-27-83	P	O	O	20 - 25	-	6.5	195	73.80	0.00	Y
Lc51-1	8-17-82	M	A	I	33 - 73	13.4	5.3	93	-	6.68	Y
Lc55-1	7-5-83	W	D	O	55 - 60	16.0	5.8	52	2.00	0.84	N
Mb14-1	10-4-82	M	D	O	? - 32	15.5	4.5	79	3.28	5.30	N
Mb22-2	6-29-83	W	A	F	36 - 40	15.0	5.2	180	4.50	8.45	Y
Mb24-1	7-5-83	W	D	O	? - 45	20.5	5.6	157	2.70	3.65	N
Mb53-1	10-25-83	P	D	W	? - 28	15.0	6.4	68	-	0.00	N
Mc13-1	10-5-82	E	D	O	? - 35	15.6	4.8	110	4.92	7.28	N
Mc22-1	4-28-83	E	D	O	? - 60	12.0	5.7	259	9.50	4.20	N

Well No.	Sample date	Soil drain-age	Use		Screened interval	Temp	pH	Sp Cond	Alk	D.O.	Lab?
Well	Sample	Soil	Well	Land	Screened	Temp	pH	Sp	Alk	D.O.	Lab?
No.	date	drain-			interval			Cond			
		age									
Mc24-2	6-22-83	M	D	O	? - 64	16.0	5.6	245	28.90	1.24	N
Mc31-3	9-11-83	W	A	I	41 - 61	14.1	6.3	132	43.00	0.00	Y
Mc51-1	5-12-83	E	O	O	15 - 19	15.5	5.5	208	9.70	4.80	Y
Md31-4	4-29-83	M	M	R	? - 55	15.5	5.9	97	18.40	6.75	Y
Md43-2	10-26-83	E	D	O	45 - 50	15.0	6.5	235	30.34	2.55	N
Md55-2	9-9-83	W	D	O	? - 50	15.1	5.8	40	12.80	3.40	Y
Nb34-4	9-9-83	P	A	F	41 - 51	19.0	5.4	118	6.00	3.05	Y
Nc14-1	9-22-83	W	D	O	? - 45	16.9	5.8	172	9.90	10.10	N
Nc22-2	10-26-83	W	D	O	? - 28	15.0	5.5	57	4.90	9.00	N
Nc25-20	5-11-83	M	M	R	? - 70	13.6	5.6	97	6.30	7.97	Y
Nc42-5	6-17-83	W	D	O	? - 55	15.3	4.7	545	2.20	2.33	N
Nc51-3	11-1-83	W	D	O	? - 36	15.0	5.4	255	16.40	4.70	N
Nd25-3	12-28-82	M	O	W	112 - 117	13.5	6.5	81	34.40	0.03	Y
	3-30-83	M	O	W	112 - 117	14.0	6.5	77	32.80	0.04	N
	7-21-83	M	O	W	112 - 117	18.5	6.3	74	32.20	0.15	N
	10-18-83	M	O	W	112 - 117	15.5	6.4	72	31.50	0.42	Y
Nd25-4	12-28-82	M	O	W	85 - 90	14.5	6.4	48	14.80	0.00	Y
	3-30-83	M	O	W	85 - 90	13.5	6.5	47	19.60	0.00	N
	7-21-83	M	O	W	85 - 90	19.0	6.2	47	15.30	0.00	N
	10-14-83	M	O	W	85 - 90	14.1	6.4	47	18.00	0.10	Y
Nd25-5	1-4-83	M	O	W	49 - 54	12.8	6.0	54	11.50	3.00	Y
	4-5-83	M	O	W	49 - 54	14.0	5.9	54	11.80	3.40	N
	7-21-83	M	O	W	49 - 54	20.0	5.8	54	10.50	4.80	N
	11-18-83	M	O	W	49 - 54	17.5	5.9	56	10.30	3.59	Y
Nd25-6	1-7-83	M	O	W	112 - 117	13.8	5.9	49	13.12	1.60	Y
	4-5-83	M	O	W	112 - 117	14.5	5.9	47	14.40	2.05	N
	7-21-83	M	O	W	112 - 117	-	5.9	47	14.40	2.73	N
	10-18-83	M	O	W	112 - 117	15.5	5.8	49	13.90	2.30	Y
Nd32-1	10-27-83	E	D	O	? - 30	14.0	5.3	144	1.60	7.80	N
Nd34-2	11-18-83	P	D	W	? - 65	14.5	5.6	31	7.40	5.80	N
Nd51-1	7-16-82	M	D	O	? - 35	14.4	5.5	38	4.10	9.41	N
Ne32-2	11-1-83	E	D	O	? - 30	14.0	5.9	62	17.20	3.10	N
Ne54-3	3-14-83	E	O	W	72 - 82	13.5	5.6	39	9.84	2.64	Y
Ne55-3	7-26-83	E	P	O	? - 35	17.0	5.1	67	4.20	0.90	N
Ob14-2	7-14-83	W	A	I	40 - 80	14.8	5.6	71	4.80	7.50	Y
Ob35-3	8-15-83	M	A	I	59 - 72	17.0	5.6	64	5.70	5.50	Y
Ob44-2	4-21-83	M	D	O	75 - 80	15.4	5.9	72	7.70	5.55	N
Oc14-10	4-21-83	W	M	R	100 - 110	15.3	5.8	59	7.50	8.50	Y
Oc25-4	9-13-82	M	A	I	56 - 96	16.0	6.0	86	7.38	11.21	Y
Oc42-4	11-1-83	E	D	O	? - 40	17.0	5.5	155	8.20	7.00	N
Od14-2	7-13-83	W	A	I	35 - 80	13.8	5.3	58	4.00	8.50	Y
Od23-7	7-14-83	W	A	I	60 - 100	13.9	5.0	180	1.90	8.98	Y
Od35-5	6-14-83	E	D	O	39 - 44	18.0	5.5	100	6.20	5.57	Y
Od43-1	11-2-83	W	D	O	? - 35	15.0	4.9	102	1.60	10.80	N
Od51-1	11-2-83	E	D	O	? - 70	17.0	4.6	230	0.00	9.10	N
Oe22-1	11-17-83	E	D	W	? - 80	11.0	5.5	80	3.40	7.10	N
Oe43-3	10-27-83	E	D	O	? - 50	15.0	5.4	153	2.50	9.00	N
Of11-1	8-4-83	P	D	W	51 - 61	20.0	6.1	65	24.50	0.30	Y
Of31-3	8-30-83	P	D	O	? - 74	16.0	5.9	162	7.50	5.10	N
Of41-1	2-9-83	E	M	R	97 - 117	15.3	6.0	59	14.76	3.10	Y
Pb15-3	11-8-83	E	D	O	? - 40	16.0	4.9	120	7.40	9.80	N
Pb35-2	8-24-82	E	A	I	33 - 89	15.5	5.6	123	0.82	9.15	Y
Pc13-3	3-10-83	E	P	O	80 - 104	14.5	5.5	94	3.28	7.90	Y

TABLE 10. Field data from wells in the unconfined aquifer -- continued.

Well No.	Sample date	Soil drain- age	Use		Screened interval	Temp	pH	Sp Cond	Alk	D.O.	Lab?
			Well	Land							
Pc32-11	3-24-83	E	I	W	78 - 104	14.5	4.9	82	2.79	4.82	Y
Pc32-12	3-24-83	E	I	W	63 - 83	14.5	5.7	97	22.96	2.59	Y
Pc51-5	11-16-83	E	D	O	60 - 65	15.0	5.6	38	7.40	1.70	N
Pd25-3	9-16-82	E	A	I	56 - 106	15.8	6.2	88	6.56	12.70	Y
Pd33-3	12-8-82	E	O	O	42 - 47	13.5	6.3	233	12.30	4.20	N
	2-18-83	E	O	O	42 - 47	14.5	5.5	206	5.74	3.58	Y
	5-4-83	E	O	O	42 - 47	15.0	5.4	257	5.40	3.64	N
	7-7-83	E	O	O	42 - 47	18.5	5.2	277	4.80	4.15	N
	10-4-83	E	O	O	42 - 47	19.5	5.2	235	3.28	4.75	Y
Pd33-4	12-8-82	E	O	O	89 - 94	14.0	6.0	87	9.84	0.65	N
	2-22-83	E	O	O	89 - 94	15.0	5.5	89	4.10	3.71	Y
	5-4-83	E	O	O	89 - 94	16.0	5.5	64	5.00	3.47	N
	7-7-83	E	O	O	89 - 94	-	5.4	71	4.40	4.25	N
	10-14-83	E	O	O	89 - 94	16.0	5.3	71	4.10	3.95	Y
Pd33-6	7-15-82	M	A	F	? - 55	14.9	5.6	82	5.74	6.75	N
Pd33-7	6-24-83	W	D	O	45 - 50	15.5	5.2	395	3.30	9.06	N
Pd45-3	9-9-82	E	A	I	50 - 100	14.3	6.1	226	6.56	11.89	Y
Pd51-3	11-8-83	E	D	O	? - 52	16.0	5.3	110	1.60	11.60	N
Pd55-2	7-13-82	E	D	O	? - 75	16.0	5.0	230	1.64	11.90	N
Pe11-2	10-7-83	E	D	W	? - 43	15.0	5.7	41	6.70	8.30	N
Pe23-48	7-22-82	M	A	I	? - 115	20.5	5.5	110	6.56	2.17	N
Pe23-49	6-23-82	M	A	I	? - 85	14.6	5.1	179	3.28	8.50	N
Pe25-2	3-5-83	W	D	O	30 - 35	15.9	5.2	212	6.30	4.90	Y
Pe53-5	11-16-83	M	D	O	? - 48	14.5	5.5	190	5.70	8.80	N
Pe54-4	11-4-83	M	O	W	123 - 130	12.0	6.1	74	28.00	0.41	Y
Pe54-9	11-4-83	M	O	W	23 - 33	13.0	5.2	31	3.77	3.70	N
Qb35-5	11-16-83	E	D	O	? - 70	14.0	5.5	112	1.60	8.90	N
Qc13-7	7-6-83	E	D	O	? - 88	16.5	4.8	154	2.46	6.81	N
Qc13-8	7-6-83	E	A	F	? - 100	17.5	4.8	168	1.64	5.49	N
Qc14-9	8-31-82	E	A	I	20 - 90	15.1	5.8	150	9.84	7.89	Y
Qc42-4	8-26-82	E	A	I	? - 109	15.7	6.1	93	6.56	11.54	Y
Qc52-6	9-8-82	E	A	I	60 - 120	14.7	5.4	43	4.76	7.39	Y
Qc54-3	11-9-83	M	D	O	? - 60	14.5	5.5	63	4.90	-	N
Qd13-1	11-2-83	E	D	O	? - 25	18.0	5.3	280	3.70	6.80	N
Qd15-1	7-27-83	E	A	I	63 - 113	16.0	5.3	89	4.20	5.70	N
Qd24-1	7-14-82	W	D	O	? - 23	14.9	4.9	226	1.64	10.35	N
Qd31-2	9-14-82	W	A	I	30 - 140	14.7	5.2	143	3.28	6.84	Y
Qd45-1	11-8-83	E	D	O	? - 50	16.0	5.8	120	9.80	2.30	N
Qe22-1	7-13-82	E	A	F	? - 90	14.5	5.1	288	3.28	7.55	N
Qe22-2	7-13-82	E	A	F	? - 125	14.9	5.5	36	4.92	8.86	N
Qe25-2	11-2-83	W	D	O	? - 65	15.0	5.9	40	8.20	2.40	N
Qe31-2	7-15-83	E	A	I	? - 83	16.1	5.2	134	3.00	8.68	Y
Qe44-3	10-28-83	E	D	O	? - 35	15.0	5.4	398	7.05	3.48	Y
Rc22-5	9-16-83	E	A	I	40 - 45	15.0	4.9	166	2.40	4.10	Y
Rd13-1	11-9-83	P	D	O	? - 65	14.5	4.7	130	-	9.60	N
Rd35-5	7-29-83	E	A	I	29 - 99	15.5	5.5	53	6.00	7.24	Y
Re12-2	11-9-83	E	D	W	? - 50	16.0	5.2	45	2.50	-	N
Re34-1	7-14-82	E	D	O	? - 55	15.6	5.5	236	3.28	7.96	N

<sup>1</sup> Bottom of screened interval estimated.

Table 11. Laboratory chemical analyses of water from wells in the unconfined aquifer.  
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 [μS, microsiemens per centimeter at 25°C; mg/L, milligrams per liter; μg/L, micrograms per liter; screened interval in feet below land surface]

Well data/constituent	units	Well Number					
		Jb31-1	Jb45-2	Jb45-3	Kb23-2	Kb42-9	Kc14-2
Sample date	-	6-9-83	6-29-82	6-28-82	9-1-83	5-27-83	8-11-83
Elevation of land surface	ft	60	61	61	55	55	60
Screened interval	ft	22-27	13-18	21-26	25-30	20-25	24-29
Specific conductance	μS	99	186	96	299	252	66
Solids, residue at 180°C	mg/L	66	134	74	226	178	59
pH	-	5.4	5.3	5.8	4.6	5.6	6.8
Alkalinity as CaCO <sub>3</sub>	mg/L	20	4.0	6.0	3.0	8.0	20
Nitrogen, total as N	mg/L	0.81	4.2	0.66	22	16	
Nitrogen, organic as N	mg/L		0.47	0.17	0.18		
Nitrogen, ammonia as N	mg/L	<0.01	0.03	0.03	0.72	<0.01	<0.01
Nitrite + Nitrate as N	mg/L	0.61	3.70	0.46	21.0	16.0	<0.10
Phosphorus	mg/L	0.08	<0.01	0.02	<0.01	<0.01	<0.01
Total organic carbon	mg/L	1.4	2.2	0.80	3.0		3.1
Hardness as CaCO <sub>3</sub>	mg/L	30	53	6	64	78	10
Hardness, noncarbonate as CaCO <sub>3</sub>	mg/L	10	49	0	61	70	0
Calcium	mg/L	9.5	10	1.5	15	16	2.0
Magnesium	mg/L	1.6	6.8	0.6	6.4	9.0	1.3
Sodium	mg/L	5.1	6.1	12	20	9.6	4.4
Potassium	mg/L	1.2	5.3	1.1	7.7	6.7	0.70
Chloride	mg/L	4.0	27	15	23	17	3.0
Sulfate	mg/L	19	36	7.0	17	8.7	8.1
Fluoride	mg/L	<0.10	0.20	<0.10	0.10	<0.10	<0.10
Silica	mg/L	20	13	25	8.6	14	19
Barium	μg/L	89	150	61	610	500	61
Beryllium	μg/L	0.5	2	<1	0.6	1	<0.5
Cadmium	μg/L	1	<1	<1	<1	2	1
Cobalt	μg/L	4	10	<3	8	3	4
Copper	μg/L	30	<10	<10	40	60	<10
Iron	μg/L	760	110	2400	27	7	180
Lead	μg/L	10	10	<10	<10	10	<10
Manganese	μg/L	16	57	16	570	48	11
Molybdenum	μg/L	10	<10	<10	<10	10	10
Strontium	μg/L	71	200	27	68	270	57
Vanadium	μg/L	6	<6	<6	<6	6	<6
Zinc	μg/L	180	290	27	40	45	<sup>1</sup> 7000
Aluminum	μg/L	<10	1400	1000	400	160	<10
Lithium	μg/L	6	<4	<4	<4	4	<4

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Table 11. Laboratory chemical analyses of water from wells in the unconfined aquifer--Continued

Well data/constituent	units	Kc41-1	Lb24-1	Lc42-1		Lc42-2		Lc51-1
Sample date	-	6-8-83	8-10-83	2-28-83	9-27-83	2-28-83	9-27-83	8-17-82
Elevation of land surface	ft	56	60	58		58		61
Screened interval	ft	27-32	13-18	50-55		20-25		33-73
Specific conductance	µS	72	71	77	79	118	172	105
Solids, residue at 180°C	mg/L	57	48	94	98	99	107	90
pH	-	5.7	5.4	6.2	5.8	5.9	5.9	5.8
Alkalinity as CaCO <sub>3</sub>	mg/L	18	8.0	34	31	29	26	8.0
Nitrogen, total as N	mg/L		2.3					7.9
Nitrogen, organic as N	mg/L		0.18	0.19	1.1	0.00	0.58	1.9
Nitrogen, ammonia as N	mg/L	0.01	0.02	0.21	0.17	0.32	0.32	0.02
Nitrite + Nitrate as N	mg/L	<0.10	2.10	<0.10	<0.10	<0.10	<0.10	6.00
Phosphorus	mg/L	0.04	<0.01	1.10	0.90	0.85	0.42	<0.01
Total organic carbon	mg/L	1.8	1.1	1.6	2.0	3.1	3.2	11
Hardness as CaCO <sub>3</sub>	mg/L	10	7	22	21	23	25	17
Hardness, noncarbonate as CaCO <sub>3</sub>	mg/L	0	0	0	0	0	0	9
Calcium	mg/L	2.6	1.6	6.3	6.2	6.4	7.0	3.6
Magnesium	mg/L	0.72	0.71	1.5	1.4	1.7	1.7	1.9
Sodium	mg/L	10	8.7	7.2	6.5	12	12	11
Potassium	mg/L	0.70	0.80	1.0	0.80	1.1	0.90	1.1
Chloride	mg/L	9.2	9.7	5.9	8.0	15	16	8.1
Sulfate	mg/L	10	0.5	29	56	5.2	6.3	2.0
Fluoride	mg/L	<0.10	<0.10	0.20	<0.10	0.20	<0.10	<0.10
Silica	mg/L	33	28	35	37	35	38	25
Barium	µg/L	86	85	43	44	62	67	120
Beryllium	µg/L	<0.5	<0.5	<1	<0.5	<1	<0.5	<1
Cadmium	µg/L	<1	<1	3	2	3	1	<1
Cobalt	µg/L	21	4	<3	55	<3	96	4
Copper	µg/L	<10	10	<10	<10	<10	<10	<10
Iron	µg/L	6400	190	13,000	16,000	27,000	30,000	<3
Lead	µg/L	10	10	<10	<10	<10	<10	30
Manganese	µg/L	68	8	130	110	130	120	9
Molybdenum	µg/L	<10	10	<10	<10	<10	<10	<10
Strontium	µg/L	43	35	74	69	85	91	93
Vanadium	µg/L	<6	<6	<6	<6	<6	<6	<6
Zinc	µg/L	150	210	13	5	3	4	13
Aluminum	µg/L	10	10	<10		<10	300	<100
Lithium	µg/L	<4	<4	<4	<4	<4	<4	<4

Mb22-2	Mc31-3	Mc51-1	Md31-4	Md55-2	Nb34-4	Nc25-20	Nd25-3	
6-29-83	9-11-83	5-12-83	4-29-83	9-9-83	9-9-83	5-11-83	12-28-82	10-18-83
62	45	55	62	56	43	50	50	
30-40	41-61	15-19	7-55	7-50	41-51	7-70	112-117	
181	124	214	102	43	120	101	76	70
133	90	168	88	63	102	91	87	74
5.4	5.9	5.3	5.7	5.1	4.8	5.4	6.3	6.1
4.0	36	9.0	18	16	10	7.0	32	29
	1.1				8.5	5.9	1.6	
	0.87						1.4	0.02
<0.01	0.13	0.01	0.02	<0.01	<0.01	<0.01	0.08	0.18
12.0	0.19	14.0	3.4	0.23	5.80	5.70	0.13	<0.10
<0.01	0.06	<0.01	<0.01	<0.01	0.01	<0.01	0.01	<0.01
3.0	1.5	3.0	2.1	3.6	1.2	7.2	3.3	5.3
51	39	62	15	6	25	20	8	9
47	3	53	0	0	15	13	0	0
8.4	12	6.7	4.4	2.0	6.1	5.7	2.3	2.6
7.3	2.1	11	0.85	0.22	2.2	1.4	0.55	0.64
8.2	6.2	5.8	12	5.4	7.3	7.8	15	10
3.9	1.2	2.7	0.90	0.40	4.4	1.9	1.1	1.0
20	5.8	19	8.2	4.2	17	10	4.9	4.5
5.0	15	0.7	2.3	0.6	0.8	0.4	<5.0	1.3
<0.10	0.10	<0.10	<0.10	<0.10	<0.10	<0.10	0.10	<0.10
16	23	9.8	29	30	18	21	33	34
170	48	440	46	34	660	120	34	40
0.7	1	<0.5	<1	1	2	<0.5	<1	<0.5
<1	<1	1	<1	<1	<1	<1	<1	<1
<3	20	8	<3	<3	7	<3	13	10
20	<10	10	<10	<10	10	30	<10	<10
39	5600	930	12	37	19	8	1400	2600
<10	<10	<10	<10	<10	<10	<10	10	<10
24	160	320	<1	1	170	4	92	140
<10	<10	<10	<10	20	<10	<10	<10	<10
200	110	79	78	55	65	92	39	49
<6	<6	<6	<6	11	<6	<6	<6	<6
46	9	<sup>1</sup> 6000	30	49	59	22	51	25
	<10	40	<10	10	100	10		10
<4	<4	<4	<4	<4	<4	8	<4	<4

Table 11. Laboratory chemical analyses of water from wells in the unconfined aquifer--Continued.

Well data/constituent	units	Nd25-4		Nd25-5		Nd25-6		Ne54-3
Sample date	-	12-28-82	10-14-83	1-4-83	10-18-83	1-7-83	10-18-83	3-14-83
Elevation of land surface	ft	50		50		50		50
Screened interval	ft	85-90		49-54		39-44		72-82
Specific conductance	$\mu\text{S}$	34	52	49	59	47	53	35
Solids, residue at 180°C	mg/L	63	56	56	59	60	54	56
pH	-	6.1	5.9	5.9	5.7	5.8	5.6	5.3
Alkalinity as $\text{CaCO}_3$	mg/L	10	11	12	14	14	16	9.0
Nitrogen, total as N	mg/L			2.4	2.5	1.4	1.7	
Nitrogen, organic as N	mg/L		0.27	0.28		0.15	0.17	
Nitrogen, ammonia as N	mg/L	0.03	0.03	0.02	<0.01	0.05	0.03	<0.01
Nitrite + Nitrate as N	mg/L	<0.10	<0.10	2.10	2.30	1.20	1.50	<0.01
Phosphorus	mg/L	0.03	0.05	<0.01	<0.01	0.01	0.01	<0.01
Total organic carbon	mg/L	1.4	2.2	1.6	0.60	1.1	0.60	1.6
Hardness as $\text{CaCO}_3$	mg/L	2	2	8	8	7	7	5
Hardness, noncarbonate as $\text{CaCO}_3$	mg/L	0	0	0	0	0	0	0
Calcium	mg/L	0.52	0.59	2.3	2.5	2.2	2.3	1.2
Magnesium	mg/L	0.13	0.17	0.44	0.45	0.34	0.36	0.35
Sodium	mg/L	5.7	7.1	6.8	7.2	6.8	6.7	4.4
Potassium	mg/L	0.40	0.50	0.90	0.90	0.80	0.80	1.2
Chloride	mg/L	5.3	5.9	4.5	4.7	4.1	4.4	5.0
Sulfate	mg/L	<5.0	1.8	2.0	0.4	<1.0	0.4	0.9
Fluoride	mg/L	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
Silica	mg/L	35	35	22	23	24	23	14
Barium	$\mu\text{g/L}$	30	52	50	55	62	66	33
Beryllium	$\mu\text{g/L}$	<1	<0.5	<1	<0.5	<1	<0.5	<1
Cadmium	$\mu\text{g/L}$	<1	<1	<1	<1	<1	<1	<1
Cobalt	$\mu\text{g/L}$	11	<3	<3	<3	<3	<3	<3
Copper	$\mu\text{g/L}$	<10	<10	<10	<10	<10	<10	<10
Iron	$\mu\text{g/L}$	3700	4300	18	16	<3	9	300
Lead	$\mu\text{g/L}$	<10	<10	<10	<10	<10	<10	<10
Manganese	$\mu\text{g/L}$	24	26	10	8	6	2	7
Molybdenum	$\mu\text{g/L}$	<10	<10	10	<10	<10	<10	<10
Strontium	$\mu\text{g/L}$	11	11	44	49	42	44	30
Vanadium	$\mu\text{g/L}$	<6	<6	<6	<6	<6	<6	<6
Zinc	$\mu\text{g/L}$	7	10	11	11	14	10	20
Aluminum	$\mu\text{g/L}$		50	60	10	10	20	10
Lithium	$\mu\text{g/L}$	<4	<4	<4	<4	<4	<4	<4

Ob14-2	Ob35-3	Ob14-10	Oc25-4	Od14-2	Od23-7	Od35-5	Of11-1	Of41-1	Pb35-2
7-14-83	8-15-83	4-21-83	9-13-82	7-13-83	7-14-83	6-14-83	8-4-83	2-9-83	8-24-83
50	48	42	45	45	41	36	49	48	30
40-80	59-72	100-110	56-96	35-80	60-100	39-44	51-61	97-117	33-89
70	69	62	96	62	177	106	63	59	144
99	98	56	109	57	148	77	31	60	91
4.9	5.0	5.7	6.3	5.4	4.8	5.6	5.9	5.8	6.0
5.0	6.0	7.0	7.0	4.0	3.0	6.0	12	12	4.0
	5.7		7.8			6.9		2.3	11
	0.15		1.2			0.09	0.11		0.53
<0.01	0.05	<0.01	0.11	0.01	0.06	0.01	0.09	<0.01	0.67
5.00	5.50	2.90	6.50	2.90	15.0	6.80	<0.10	1.80	10.0
0.02	0.04	<0.01	0.02	0.02	0.02	<0.01	0.04	<0.01	0.01
1.3	1.1	2.5	1.2	1.6	1.8	3.0	2.3	0.40	1.0
10	10	8	18	10	47	20	2	10	35
5	4	1	11	6	44	14	0	0	34
2.4	2.5	2.2	4.1	1.8	7.9	5.3	0.33	2.8	5.6
1.0	0.83	0.63	1.8	1.2	6.5	1.6	0.36	0.59	5.0
6.4	8.9	6.2	8.5	5.3	8.8	8.5	5.9	6.7	5.7
2.0	2.2	1.7	3.1	2.3	3.9	2.6	1.0	1.3	2.8
8.1	4.9	6.3	8.8	6.3	13	9.3	7.4	5.8	9.3
0.8	0.3	3.0	<1.0	1.1	0.4	6.0	2.7	<5.0	2.0
<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
19	19		18	12	11	12	8.7	28	14
73	140	72	190	230	680	210	86	62	370
0.6	<0.5	<0.5	<1	<0.5	1.7	<0.5	<0.5	<1	<1
<1	<1	<1	4	<1	<1	<1	<1	<1	3
<3	<3	<3	<3	<3	<3	<3	<3	<3	<3
<10	<10	<10	<10	<10	20	10	<10	<10	20
<3	13	12	48	19	<3	37	12,000	67	27
10	<10	<10	10	<10	<10	<10	<10	<10	<10
5	1	2	11	12	120	10	57	7	59
<10	<10	<10	<10	<10	<10	<10	<10	<10	<10
66	62	48	94	48	160	110	16	36	150
<6	<6	<6	<6	<6	<6	<6	<6	<6	<6
9	23	81	180	17	14	86	220	320	46
10	<10	10	<100	10	90	20	<10	<10	<100
<4	<4	<4	<4	<4	<4	<4	<4	<4	<4



Table 11. Laboratory chemical analyses of water from wells in the unconfined aquifer--Continued.

Well data/constituent	units	Pc13-3	Pc32-11	Pc32-12	Pd23-3	Pd33-3
Sample date	-	3-10-83	3-24-83	3-24-83	9-16-82	2-18-83 10-4-83
Elevation of land surface	ft	33	22	12	32	35
Screened interval	ft	80-104	78-104	63-86	56-106	42-47
Specific conductance	$\mu$ S	90	81	101	80	204 246
Solids, residue at 180°C	mg/L	84	68	70	60	135 177
pH	-	5.4	4.7	5.4	6.1	5.5 5.2
Alkalinity as CaCO <sub>3</sub>	mg/L	4.0	3.0	21	6.0	7.0 7.0
Nitrogen, total as N	mg/L		3.8	2.0	5.7	
Nitrogen, organic as N	mg/L		0.05	0.10	1.3	
Nitrogen, ammonia as N	mg/L	0.02	0.25	1.30	0.08	0.02 0.01
Nitrite + Nitrate as N	mg/L	6.40	3.50	0.59	4.30	16.0 20.0
Phosphorus	mg/L	0.02	0.06	0.07	<0.01	0.01 <0.01
Total organic carbon	mg/L	1.8	2.5	2.5	0.70	0.40 5.6
Hardness as CaCO <sub>3</sub>	mg/L	23	16	11	18	39 58
Hardness, noncarbonate as CaCO <sub>3</sub>	mg/L	19	13	0	13	32 51
Calcium	mg/L	5.3	2.4	1.9	3.2	10 15
Magnesium	mg/L	2.2	2.4	1.5	2.3	3.2 4.8
Sodium	mg/L	5.4	4.9	9.5	5.2	16 20
Potassium	mg/L	1.9	2.0	2.2	2.1	4.0 4.1
Chloride	mg/L	8.1	5.9	7.7	6.6	15 18
Sulfate	mg/L	3.6	8.9	10	<1.0	<5.0 1.4
Fluoride	mg/L	<0.10	<0.10	<0.10	<0.10	<0.10 <0.10
Silica	mg/L	14	7.5	8.9	15	17 18
Barium	$\mu$ g/L	99	150	65	110	270 440
Beryllium	$\mu$ g/L	1	<1	<1	<1	<1 <0.5
Cadmium	$\mu$ g/L	1	<1	<1	<1	2 <1
Cobalt	$\mu$ g/L	3	4	4	<3	17 10
Copper	$\mu$ g/L	10	30	<10	<10	<10 <10
Iron	$\mu$ g/L	11	43	1600	17	17 35
Lead	$\mu$ g/L	10	<10	<10	<10	<10 <10
Manganese	$\mu$ g/L	9	56	110	78	200 130
Molybdenum	$\mu$ g/L	10	<10	<10	<10	<10 <10
Strontium	$\mu$ g/L	110	35	25	78	260 330
Vanadium	$\mu$ g/L	6	<6	<6	<6	<6 <6
Zinc	$\mu$ g/L	15	34	14	54	62 57
Aluminum	$\mu$ g/L	<10	150	20	<100	20 10
Lithium	$\mu$ g/L	4	<4	<4	21	<4 <4

Pd33-4		Pd45-3	Pe25-2	Pe54-4	Qc14-9	Qc42-4	Qc52-6	Qd31-2	Qe31-2
2-22-83	10-14-83	9-9-82	8-5-83	11-4-83	8-31-82	8-26-82	9-8-82	9-14-82	7-15-83
35		40	48	51	30	40	42	30	35
89-94		50-100	30-35	123-130	20-90	7-109	60-120	30-140	7-83
79	71	236	214	81	150	118	65	144	152
74	70	188	135	68	48	110	48	115	147
5.6	4.6	5.9	5.1	5.6	5.4	8.5	5.9	5.7	5.5
5.0	9.0	6.0	6.0	24	2.0	6.0	9.0	5.0	3.0
5.8		19	7.0		14		3.1	8.6	
		0.26			0.47		0.68	0.97	
<0.01	0.02	0.04	<0.01	0.08	0.03	<0.01	0.02	0.03	<0.01
5.70	4.50	19.0	6.60	<0.10	13.0		2.40	7.60	12.0
<0.01	0.01	<0.01	0.02	<0.01	<0.01	<0.01	<0.01	0.01	0.03
1.1	0.80	2.8	3.3	1.0	0.80		0.80	0.80	2.0
14	11	65	33	14	46	26	11	35	38
9	2	59	27	0	44	20	2.0	30	35
3.9	3.2	17	6.4	3.8	5.8	4.6	2.6	8.6	9.4
0.95	0.73	5.3	4.1	1.1	7.4	3.3	0.9	3.2	3.5
9.1	9.4	11	24	9.0	6.1	6.7	4.8	8.4	7.9
2.2	1.6	3.4	2.7	0.90	4.1	3.2	1.6	1.8	2.3
7.2	7.4	18	19	7.8	2.7	9.2	6.0	9.6	11
<5.0	1.7	1.0	32	1.8	40	<1.0	2.0	12	0.5
<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
21	20	17	11	31	11	17	16	23	14
110	120	300	140	54	630	400	130	140	330
1.1	<0.5	<1	<0.5	<0.5	1.7	<1	<1	<1	0.6
<1	<1	2	<1	<1	1	<1	<1	<1	<1
7	6	<3	<3	<3	11	<3	<3	3	<3
<10	<10	<10	90	<10	20	<10	<10	<10	<10
13	15	<3	120	2600	46	45	<3	450	9
<10	<10	10	20	<10	10	<10	<10	10	<10
140	74	17	24	120	65	100	12	31	22
<10	<10	<10	<10	<10	10	<10	<10	<10	<10
64	53	430	110	63	170	150	73	150	230
<6	<6	<6	<6	<6	8	<6	<6	<6	<6
13	22	49	190	89	95	87	30	31	28
40	30	<100	<10	<10	200	300	<100	100	<10
<4	<4	<4	<4	7	8	<4	<4	<4	4

Well data/constituent	units	Qe44-3	Rc22-5	Rd35-5
Sample date	-	10-28-83	9-16-83	7-29-83
Elevation of land surface	ft	45	44	55
Screened interval	ft	?-35	40-45	22-99
Specific conductance	µS	420	182	53
Solids, residue at 180°C	mg/L	318	129	84
pH	-	5.3	4.9	5.5
Alkalinity as CaCO <sub>3</sub>	mg/L	9.0	6.0	7.0
Nitrogen, total as N	mg/L	21	14	2.0
Nitrogen, organic as N	mg/L	0.26	0.29	
Nitrogen, ammonia as N	mg/L	0.34	0.01	<0.01
Nitrite + Nitrate as N	mg/L	40.0	14.0	1.90
Phosphorus	mg/L	0.03	0.01	0.05
Total organic carbon	mg/L	1.1	1.6	0.80
Hardness as CaCO <sub>3</sub>	mg/L	140	50	8
Hardness, noncarbonate as CaCO <sub>3</sub>	mg/L	130	44	1
Calcium	mg/L	32	10	0.98
Magnesium	mg/L	14	5.9	1.4
Sodium	mg/L	11	7.8	5.0
Potassium	mg/L	8.0	4.0	1.8
Chloride	mg/L	15	16	7.3
Sulfate	mg/L	6.7	1.2	0.4
Fluoride	mg/L	0.10	<0.10	0.10
Silica	mg/L	20	14	14
Barium	µg/L	710	610	210
Beryllium	µg/L	1.7	1.2	<0.5
Cadmium	µg/L	<1	1	<1
Cobalt	µg/L	32	4	<3
Copper	µg/L	<10	<10	<10
Iron	µg/L	23	14	<3
Lead	µg/L	<10	<10	<10
Manganese	µg/L	250	35	13
Molybdenum	µg/L	<10	<10	<10
Strontium	µg/L	690	360	42
Vanadium	µg/L	<6	<6	<6
Zinc	µg/L	110	42	8
Aluminum	µg/L	40	<10	10
Lithium	µg/L	7	10	<4

<sup>1</sup> Zinc concentration is high because of chemical reaction with galvanized casing.

## APPENDIX II

## APPENDIX II

## CONVERSION FACTORS

For readers who prefer to use metric (International System) units, factors for converting the inch-pound units used in this report to metric units are listed below:

<u>Multiply inch-pound unit</u>	<u>By</u>	<u>To obtain metric unit</u>
foot (ft)	0.3048	meter (m)
foot per day (ft/d)	0.3048	meter per day (m/d)
foot squared per day (ft <sup>2</sup> /d)	0.0929	meter squared per day (m <sup>2</sup> /d)
foot per mile (ft/mi)	0.1894	meter per kilometer (m/km)
gallon per minute (gal/min)	0.0630	liter per second (L/s)
gallon per day (gal/d)	3.785	liter per day (L/d)
million gallons per day (Mgal/d)	0.04381	cubic meter per second (m <sup>3</sup> /s)
inch (in.)	25.40	millimeter (mm)
square mile (mi <sup>2</sup> )	2.590	square kilometer (km <sup>2</sup> )